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APPLICATION OF THE PSEUDOADIABATIC REACTOR TO THE CONVERSION OF SYNTHESIS GAS INTO BLENDING STOCKS.

FINAL REPORT

by

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SUMMARY

A bi-functional catalyst was successfully developed at the Chemical Reactor Engineering Centre, University of Western Ontario with the dual function of methanol synthesis and methanol conversion. Based on test carried out in a Berty reactor the following catalyst composition was chosen: 63% Zn/Cr (25/75 atomic ratio), 27% H-ZSM-5 and 10% Versal 950 Al_2O_3 binder. The transformation of synthesis gas takes place on the dual MSC/ZSM-5 catalyst with a "drain-off" effect, e.g. methanol is formed and readily converted on the zeolite component. This catalyst demonstrated very high selectivity for aromatics hydrocarbons while producing little amount of methane. The catalyst was characterized using XRD and BET. Some valuable insights were obtained about the states of the zinc and chrome as well as on the role of the oxides of these two metals.

A kinetic model for the conversion of synthesis gas was also developed and tested with experimental data obtained in a Berty well-mixed reactor.

A pilot plant unit used extensively for the conversion of methanol in a previous project was modified and adapted for the conversion of synthesis gas. A number of runs were developed in the pilot plant unit to confirm the possible application of the novel Pseudoadiabatic Reactor concept for the selective conversion of synthesis gas into hydrocarbons (gasoline range). Typical conditions of operations were: 20-34 atm and 350-400°C. This allows to speculate about the special advantages of this system (capital cost savings) for hydrocarbons synthesis at moderated pressure. It was observed that the Pseudoadiabatic Operation was obtained consistently for most of the runs which indicates simple design of the unit and simple rules for scaling-up. Another

finding of particular interest were the CO converted into liquid hydrocarbons that ranged between 12 to 17%. In some of the runs, this hydrocarbons had C_5^+ fraction (mainly aromatics) reaching values as high as 73% of the total hydrocarbons produced. Besides, the methane fraction in the hydrocarbons was found to be very low (<4.5%).

The present program also involved significant activities in the area of reactor modelling. It was observed that the predictions of reactor regime (Pseudoadiabatic, non-Pseudoadiabatic) using the kinetic model for the bi-functional catalyst and computer simulation confirmed experimental observations in the pilot plant.

This research contract also included the development of a kinetic models for the methanol to gasoline reaction on ZSM-5 and the conversion of synthesis gas on two catalysts provided by CANMET.

RESUME

Un catalyseur bifonctionnel pour la transformation sélective du gas de synthèse en essence à moteur a été développé avec succès au Centre de Génie des Réacteurs Chimiques de l'Université Western Ontario. Le catalyseur bifonctionnel a la double capacité de synthétiser le méthanol et de le convertir en essence à moteur. Des essais catalytiques réalisés avec un réacteur de type Berty a permis de déterminer la composition optimale suivante du catalyseur: 63% ZnO/Cr_2O_3 (rapport atomique Zn/Cr=25/75), 27% H-ZSM-5 and 10% liant alumine Versal 950. La transformation du gas de synthèse a lieu sur le catalyseur bifonctionnel avec un effet "drain-off" très prononcé e.i. aussitôt que le méthanol est formé, il est converti en essence à moteur. Ce catalyseur a démontré une sélectivité importante pour les hydrocarbures de type aromatique ainsi que très peu d'activité pour la méthanation. Une caractérisation du catalyseur a aussi été réalisée utilisant les techniques de diffraction des Rayons-X et de mesures de surface spécifique (BET). Beaucoup d'information concernant l'état physico-chimique du zinc et du chrome ainsi que leurs rôles en tant qu'oxides a été obtenue.

Un modèle cinétique a aussi été développé pour la conversion du gas de synthèse en essence à moteur utilisant le réacteur de type Berty.

Une unité pilote, déjà étudiée pour la conversion du méthanol lors d'un projet antérieur, a été modifiée et adaptée pour la conversion du gas de synthèse en essence à moteur. Plusieurs essais ont été réalisés avec cette unité pour confirmer le nouveau concept d'opération Pseudoadiabatique. Ces essais ont aussi servi à démontrer les avantages économiques (investissement initial et coûts d'opération) de l'utilisation de ce système pour la synthèse d'essence à moteur à pression modérée. Ces essais ont été réalisés à des pressions ne dépassant pas 34 atm et à des températures variant entre 350°C et 400°C.

Le régime d'opération Pseudoadiabatique a été obtenu de façon consistante pour la plupart des essais. Une autre observation intéressante concerne la quantité de CO transformée en hydrocarbures liquides. Il a été trouvé que cette quantité variait de 12 à 17% et que pour certain essais, représentait jusqu'à 73% du total des hydrocarbures produits. La fraction de méthane a aussi toujours été très faible (<4.5%).

Le présent programme de recherche impliquait également la simulation du réacteur étudié. Il a été observé que les prédictions du régime d'opération (Pseudoadiabatique, non-Pseudoadiabatique), utilisant le modèle cinétique développé dans ce projet, confirmaient les résultats obtenus avec l'unité pilote.

Ce projet de recherche a aussi inclus le développement de modèles cinétiques pour la conversion du méthanol en essence à moteur sur ZSM-5 et la conversion du gas de synthèse sur deux catalyseurs fournis par CANMET.

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SECTION I

Introduction

I. Introduction

Several groups around the world have been carrying out research on the methanol-to-gasoline conversion process. From these studies it becomes apparent that the methanol-to-gasoline process will not be economical for several years. With about 80% of the cost of synthetic gasoline production related to the cost of methanol there is little room for improving the economics of this process.

Another approach which is already being considered is to develop suitable catalysts for the direct conversion of synthesis gas into gasoline. While some progress has been reported, there is still no feasible commercial process. Most of the research has focussed on the development of bi-functional or multi-functional catalysts with one function converting the syngas into an intermediate and the other converting the intermediate species into gasoline. This approach have met with limited success because some of the catalyst selected bifunctional catalysts involving a Fischer-Tropsch component and a ZSM5 component. These formulations can only provide poor selectivities of the desired hydrocarbons. In fact in the synthesis gas conversion complex reaction network on a bifunctinal catalyst of the FT/ZSM-5 type, the step of condensation of α-olefins, intermediate species in the Anderson-Shulz-Flory chain growth mechanism proposed for the Fischer-Tropsch catalytic function, can be considered as a competitive reaction with respect to the further condensation of α-olefins giving waxes. Then with this type of catalyst a poor selectivity can be expected.

There is however, another possible and more promising approach for bi-functional catalysts based on methanol synthesis component and methanol conversion component. Compared to the competitive reaction network expected for the Fischer-Tropsch/ZSM-5 bifunctinal catalyst, this approach can be considered as a serial reaction mechanism where the very selective methanol synthesis on the ZnO-Cr_2O_3 (initial step) is followed by the conversion of methanol on ZSM-5. The difficulty here, is given by the fact that the optimum temperatures for the formation and conversion of the intermediate key chemical species are different. Because of this limitation, the best results have been obtained with dual catalytic reactors where the functions of methanol synthesis and methanol conversion were separated rather than integrated in a single reactor unit.

The recent successful development at the Chemical Reactor Engineering Centre, University of Western Ontario of the Pseudoadiabatic Catalytic Reactor for exothermic chemical transformations offers new possibilities for using bi-functional catalysts converting synthesis gas into valuable hydrocarbon products. It is shown in the present research contract that a good control of the reactor temperature provides adequate catalyst performance for both functions, methanol synthesis and methanol conversion, allowing promising yields of high octane gasoline. Furthermore, the present project also establishes that the catalyst design based on the "drain-off" effect keeps the methanol synthesis reaction far from equilibrium. This was observed both in the Berty reactor experiments and in the pilot plant unit. Then, the high pressure for methanol production, needed in dual bed approach (one for methanol synthesis and one for methanol conversion), is not a requirement any more in the Pseudoadiabatic Reactor unit. This result shows excellent possibilities for reducing the capital cost of the synthesis gas conversion process, making it economically viable for the production of high octane gasoline. Also a steam reformer producing synthesis gas from methane with CO/H_2 ratio of 1 (optimum ratio in this study) instead of

2 or 3 would reduce significantly the investment and operating cost for this unit (Teuner, 1987; Goff et al., 1987; Dibbern et al., 1986).

The research contract program described in this report was organized as follows:

- Preparation, pre-treatment and characterization of the catalysts developed at the University of Western Ontario. In Section II the various methods and steps of catalyst preparation including co-precipitation, wet impregnation, drying, calcination and reduction are reviewed.

- Reaction experiments in a Berty reactor. This involved exploratory runs and reaction runs with a ZSM5 catalyst, several bi-functional catalysts prepared at the University of Western Ontario and two catalysts developed at CANMET. Systematic runs with the ZSM5 catalysts and bi-functional catalysts, prepared at the University of Western Ontario, were also developed in order to allow proper kinetic modelling. The various aspects of these runs are described in Section III.

- Re-design of Pseudoadiabatic Reactor pilot plant unit. These activities involved modifiying the existing experimental set-up and the different accessories of the reactor as required by the new operating conditions for synthesis gas conversion: e.g. higher temperature (400°C) and higher pressure (50000 KPa). The description of the various tasks performed are reported in Section IV.

- Runs in pilot plant unit using a bifunctional catalyst to study the conditions of Pseudoadiabatic Operation. For these runs the temperature profiles, conversion of synthesis gas, hydrocarbon product distribution were measured. Assessments were also performed to establish catalyst deactivation. These various aspects of the program are covered in Section V.

- Simulation of the Pseudoadiabatic Reactor. The program was completed with a number of computer simulation activities where the kinetic model and kinetic parameters determined in the Berty reactor were integrated with a pseudohomogeneous unidimensional model to assess the regime of pilot plant operation, outlet synthesis gas conversions and heat transfer coefficients in the bed. The different results are discussed in Section VI.

In summary, the present research contract addresses a challenging research program. With the results presented in this report the potential and value of the Pseudoadiabatic Reactor combined with a bi-functional catalyst is demonstrated for the conversion of synthesis gas into hydrocarbons (gasoline range).

SECTION II

Catalyst Preparation and Characterization

A. Synthesis and Characterization of ZSM-5 Zeolite

B. Preparation and Characterization of Ag-ZnO Catalyst

C. Preparation and Characterization of Bifunctional Catalyst

II. Catalyst Preparation and Characterization.

A. Zeolite ZSM-5.

1) Synthesis

A batch of 1.1 kg of ZSM-5 in its precursor state (TPA$^+$, Na$^+$ -ZSM-5) has been synthesised over a period of 7 days, continuously at 160°C, in a 3.7 gallon stirred autoclave. The method followed was proposed by Gabelica et al. (1983). A fully detailed description of the method is given in Appendix A.

A fraction of the washed precursor zeolite was then mixed with an α-pseudoboehmite alumina binder Versal 950 from Kaiser Chemicals and, to fused alumina inert particules. Deionized water was added to this powder mixture in order to form a paste which was then extruded into 1/8" cylindrical pellets. After drying at 110°C, the pellets were calcined at 530°C for 16 hours. The targetted weight composition of the pellets was :

25% H-ZSM-5
30% Al_2O_3 binder
45% fused Al_2O_3 diluent

The calcined pellets were ion-exchanged four times with an ammonium nitrate (NH_4NO_3) solution, under the following conditions:

- 1st and 2nd ion-exchange: 3.5 liters of a 1.5 M NH_4NO_3 solution, at 80°C, for 16 hours
- 3rd and 4th ion-exchange: 3.5 liters of a 1 M NH_4NO_3 solution, at 20°C, for 16 hours.

After the last ion-exchange, the pellets were thoroughly washed with deionized water. At this stage, the zeolite in the pellets is under the ammonium form: NH_4^+-ZSM-5.

Finally, the pellets were calcined at 400°C for 3 hours, 450°C for 16 hours and 530°C for 3 hours to obtain the active form of the zeolite: H^+-ZSM-5 by elimination of NH_3. The final weight of the active pellets was: 1050 grams.

2) Characterization

An X-ray diffraction spectrum of a ZSM-5 sample in its precursor state was obtained in the Department of Materials Engineering at the UWO. The spectrum displayed well-resolved and sharp peaks, characteristic of the ZSM-5 zeolite, showing that the batch produced was highly crystalline ZSM-5 zeolite.

Atomic absorption analysis of the activated pellets, digested in a HCl + HF aqueous solution was done in the Geotechnical Research Center, at the UWO, to determine the residual Na^+ level in the catalyst. A level of 0.006 ppm of Na were found in the activated pellets, indicating that the washing and ion-exchange procedures were efficient.

Moreover, the chemical analysis of the zeolite and the pellets were done by X-ray fluorescence (XRF) in the Department of Geology at the UWO. The results are given in Table 1. The high LOI (Loss on Ignition) value shown by the zeolite in its precursor state resulted mainly from the presence of the template organic base, tetrapropyl-ammonium ion (TPA^+), used for the zeolite synthesis. The calculated silica to alumina molecular ratio (SiO_2/Al_2O_3) of the ZSM-5 zeolite

	Pellets activated state	ZSM-5 precursor state
SiO_2	23.01 ± 0.20	83.90
Al_2O_3	73.77 ± 0.20	3.40
Na_2O	0.15 ± 0.10	2.22
TiO_2	0.00 ± 0.01	0.00
MgO	0.15 ± 0.05	0.36
Fe_2O_3	0.08 ± 0.01	0.02
K_2O	0.02 ± 0.01	0.01
LOI	2.9 ± 0.30	10.40

LOI: Loss on Ignition (1100°C)

Table 1: X-ray Fluorescence Analysis of the Zeolite ZSM-5 Synthesized and the pellets prepared (weight %).

is 42, while the content of active ZSM-5 in the pellets, deduced from the silica content in both the zeolite and the pellets, is 25.4 % wt.

The macro-pore size distribution of the pellets was determined by mercury porosimetry in the Geotechnical Research Center at the UWO. The incremental pore volume as a function of pore diameter (Figure 1) shows that the pellets have a bimodal pore size distribution, at the exclusion of the zeolite pore system. A macroporous system with pore sizes averaging 5.3 μm and a system of mesopores with pore size under 100 Å can be identified. The internal volume corresponding to pores with a diameter larger than 60 Å (lowest size of pore accessible by mercury porosimetry) is 0.30 cm^3/g, with a total pore surface area (calculated on the assumption that the pores are cylindrical) of 50 m^2/g.

B. Ag-ZnO catalyst

1) Synthesis

A batch of Ag-ZnO with a 22/78 Ag/Zn atomic ratio was synthetized following a procedure similar to the one described in the literature for the preparation of Cu-ZnO catalyst, i.e. by coprecipitation of carbonate salts of Ag^+ and Zn^{2+} from a aqueous solution of their nitrate salts with a sodium carbonate solution.

A solution of zinc and silver nitrates was prepared by mixing 121 ml of a 1 M $AgNO_3$ solution and 430 ml of a 1 M $Zn(NO_3)_2.6H_2O$ solution. While maintaining the solution at 85°C under agitation, 532 ml of a 1M solution of Na_2CO_3 was added slowly, the pH of the solution reaching a value of 7. A precipitate with a light yellow colour was formed. The solution was cooled down while stirring for 2 hours. The pH of the solution then stabilized at 7.9.

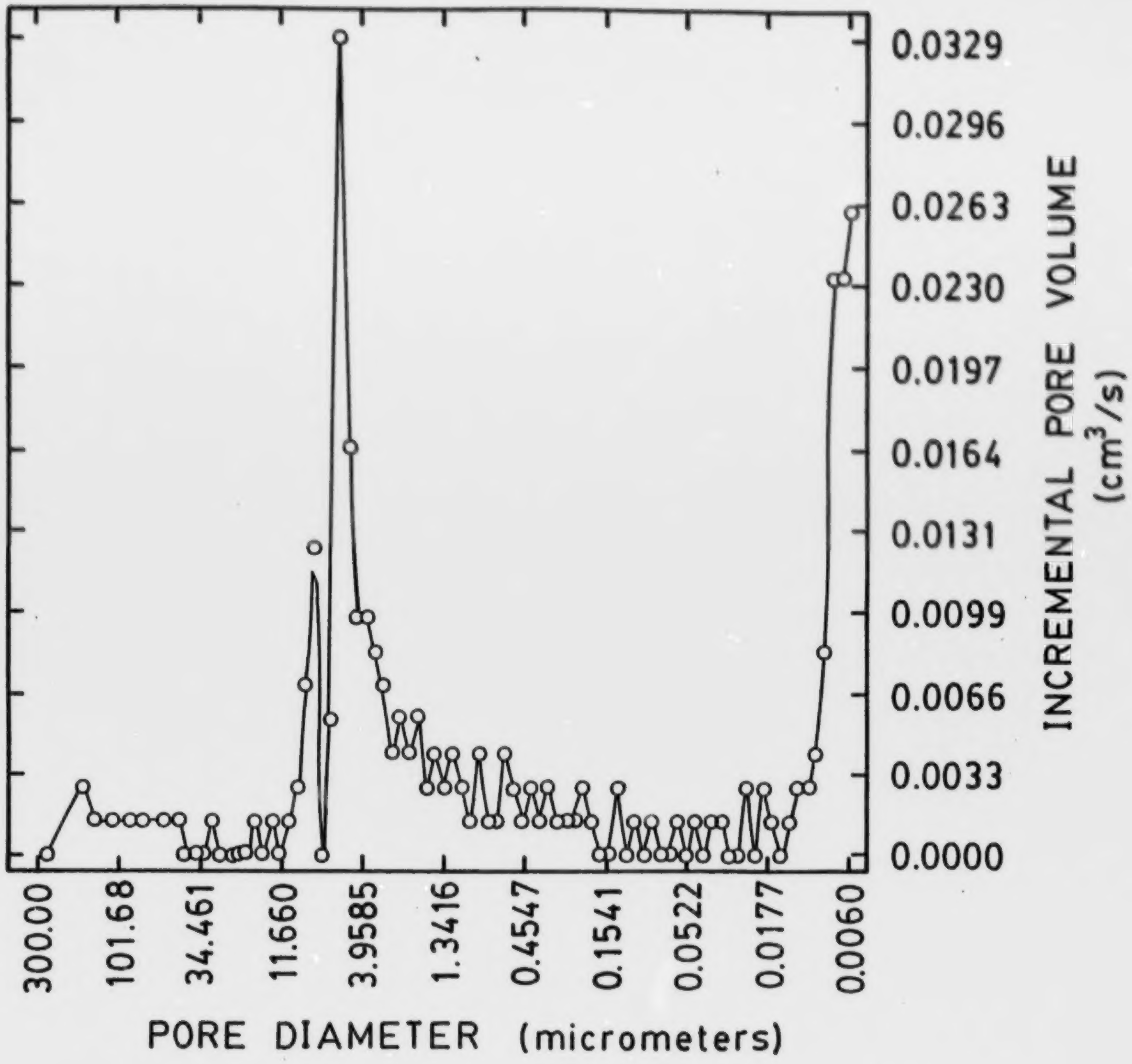


Figure 1: Pore size distribution of the ZSM-5 pellets.

The precipitate was filtered and washed with 20 liters of deionized water. It was observed that, at this stage, the surface of the cake exposed to the light turned grey-black due to the presence of silver salts. It was speculated that, the original yellow colour observed could come from the silver carbonate, Ag_2CO_3, which is known to turn black when exposed to the light (Pascal 1959a).

The cake was dried at 110°C, then calcined at increasing temperatures, starting from 150°C up to 350°C by 50°C increments, each temperature level being maintained for 30 minutes. The final weight of Ag-ZnO batch prepared was 45.5 grams.

2) Characterization

X-ray diffraction spectra of the precipitate precursor (dry state) and of the calcined Ag-ZnO catalyst are shown in Figure 2.

The dry precipitate displays sharp and intense peaks characteristic of Ag_2CO_3. The remaining peaks, shorter but broader, could be attributed to an hydroxy-carbonate form of Zn, most probably $Zn_5(CO_3)_2(OH)_6$. Few small but sharp peaks could come from silver metal Ag, result of the decomposition of silver carbonate when exposed to light (Pascal 1959a).

When calcined, the sample displays diffraction peaks of metallic silver and, of ZnO. The Zinc oxide phase appears to be in a more dispersed state, as indicated by its broader diffraction peaks compared to those of the Ag phase. The presence of metallic silver rather than silver oxide AgO was expected, AgO

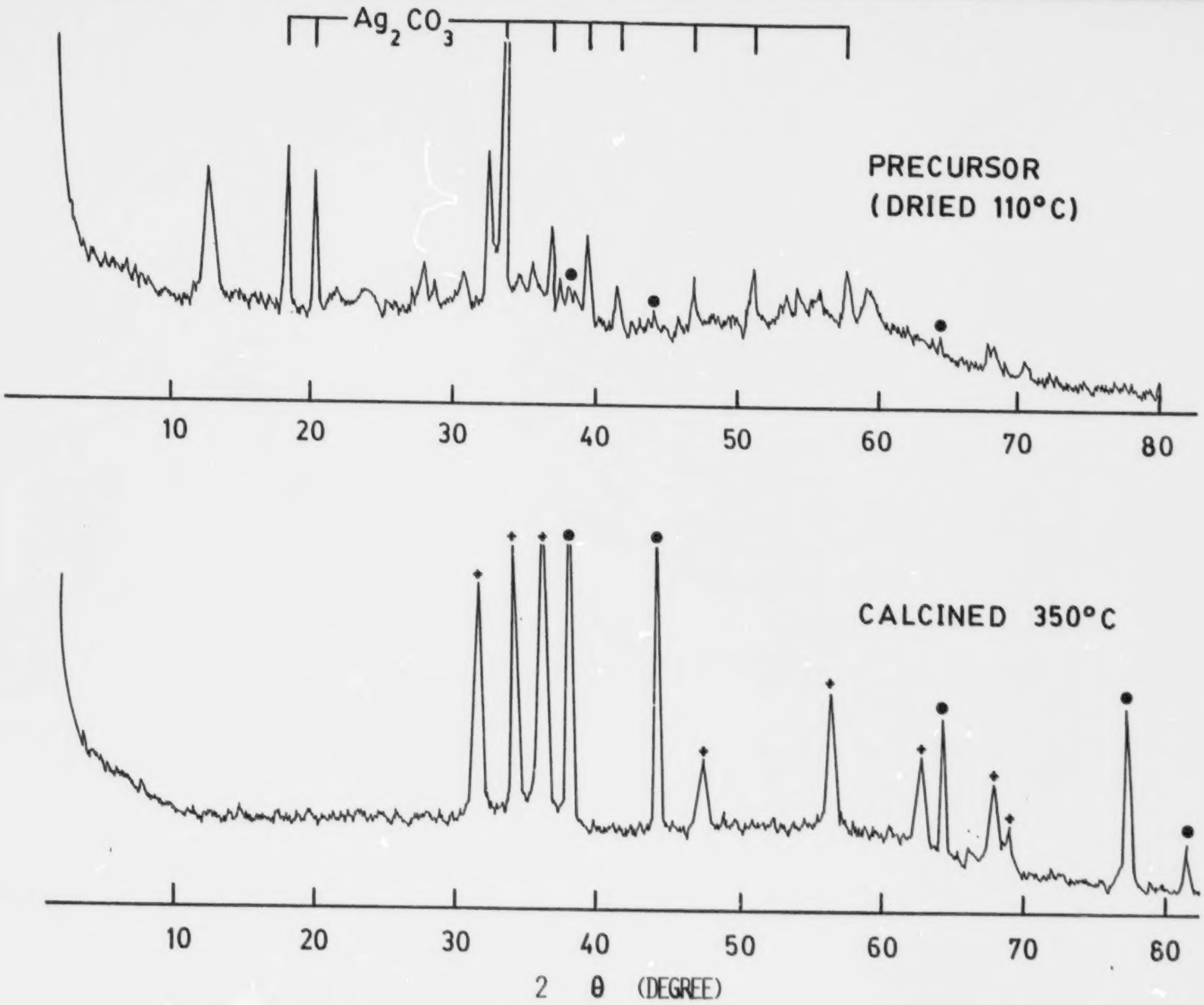


Figure 2: X-Ray Diffraction Spectra of Ag-ZnO catalyst (Ag/Zn = 22/78) dry and calcined (. : Ag metal phase; + : ZnO phase).

being decomposed into silver and oxygen at temperature higher than 100°C (Pascal 1959a).

C. $ZnO-Cr_2O_3$ catalysts.

1) Synthesis

a) Co-precipitation Method

Three samples with Zn/Cr atomic ratio of 75/25, 50/50 and 25/75 were prepared.

The hydroxydes of Zinc and Chromium were co-precipitated from solutions of zinc and chromium nitrates of different relative concentrations with an aqueous ammonia solution at 80°C. The precipitates were then filtered and washed with deionized water by repeated decantation until the wash water was found, by testing with diphenylamine reagent, free of nitrate ions. Finally, the cake was dried at 110°C overnight.

After selection of the Zn/Cr atomic ratio which gave the best catalytic performances, a second batch of 1370 grams of $ZnO-Cr_2O_3$ catalyst with a 25/75 Zn/Cr ratio was prepared for the operation of the fixed-bed pilot reactor. Given the high water retention of the precipitate, the first filtration and drying steps were extremely slow. Numerous washing cycles were needed. As a consequence, this method of synthesis was found to be quite time consuming. This preparation is referred to as 'october 87' batch.

b) Commercial Method (wet Impregnation).

In order to cut down the time needed for the catalyst synthesis, the method currently used to produce commercial $ZnO-Cr_2O_3$ catalyst (Zn/Cr > 2/1) (Stiles, 1984), was followed to synthetize a $ZnO-Cr_2O_3$ sample with a 25/75 atomic ratio. This method consists into mixing dry powders of ZnO and chromic acid anhydre (CrO_3). Deionized water was added to this dry mixture to produce a heavy paste which was subsequently kneaded for 60 minutes. The paste was then dried at 110°C and, calcined at 400°C. The solid, finally ground to a fine powder, was ready to be admixed with the zeolite.

This method does not involve any filtration and washing, and require only one day for the preparation of the catalyst. However, the main drawback of this technique was the eventuality of a bad intermixing of the Zinc and Chromium oxide phases, relatively to the co-precipitation method. Nevertheless, from the comparative diagram of the two methods, shown in Figure 3, it is obvious that the commercial method (wet impregnation) is economically more advantageous in terms of reagent costs and preparation time.

c) Preparation of the Composite Catalyst.

Two methods of preparation were employed: the tableting or dry compression method, and the extrusion, using an Al_2O_3 binder.

For most of the preliminary syngas conversion runs, conducted in the Berty reactor, the samples were prepared according to the dry compression method. The two catalytic active components, H-ZSM-5 and the methanol synthesis catalyst

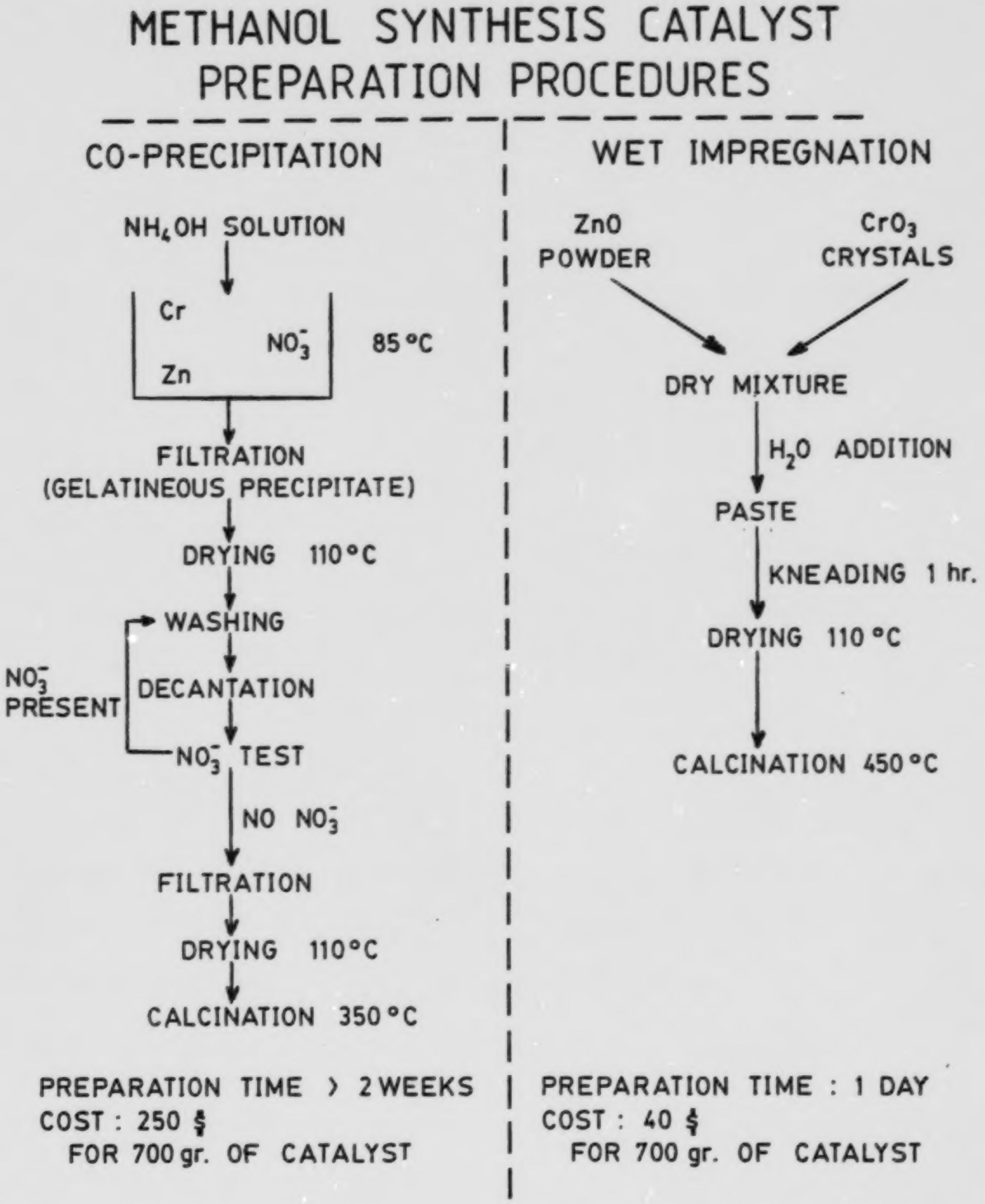

METHANOL SYNTHESIS CATALYST
PREPARATION PROCEDURES
CO-PRECIPITATION
NH₄OH SOLUTION
Cr
NO₃⁻
Zn
85 °C
FILTRATION
(GELATINEOUS PRECIPITATE)
DRYING 110 °C
WASHING
NO₃⁻
PRESENT
DECANTATION
NO₃⁻ TEST
NO NO₃⁻
FILTRATION
DRYING 110 °C
CALCINATION 350 °C
PREPARATION TIME > 2 WEEKS
COST : 250 $
FOR 700 gr. OF CATALYST
WET IMPREGNATION
ZnO
POWDER
CrO₃
CRYSTALS
DRY MIXTURE
H₂O ADDITION
PASTE
KNEADING 1 hr.
DRYING 110 °C
CALCINATION 450 °C
PREPARATION TIME : 1 DAY
COST : 40 $
FOR 700 gr. OF CATALYST

Figure 3: Comparative Diagram of $ZnO-Cr_2O_3$ Preparation Methods.

(MSC), were mixed together in a mortar into a well homogeneized dry powder mixture. This powder mixture was then compressed into a 1"1/4 diameter pellet under 16000 psi. This pellet was finally broken into granules with a 1/8" average size.

However, the pellets prepared by dry compression will not be hard enough to be used in the pilot fixed-bed reactor. Higher compaction pressures should be employed but the appropriate equipment was not available. As a consequence, the use of the extrusion method with the addition of an alumina binder was considered. This technique has the advantage of a relatively easy preparation of well shaped 1/8" cylindrical pellets. However, the density of the catalyst prepared by extrusion is much lower, as compared to the density of the pellets which could be obtained by tableting. Besides this point, the MSC component is partially attacked by the residual acidity of the pseudoboehmite binder. In order to limit this effect, which could be detrimental to the catalyst activity, the pellets were quickly dried at 110°C, after being extruded.

About 1000g of composite catalyst pellets were prepared for the pilot reactor, with the following composition:

- 63% $ZnO-Cr_2O_3$ methanol synthesis catalyst with a 25/75 Zn/Cr ratio, calcined at 350°C for 2 hours;
- 27% H-ZSM-5;
- 10% Versal 950 alumina binder.

After mixing small quantities of the three components, water was added to the powder mixture and, the resulting paste was immediately extruded. Then, the pellets were quickly dried at 110°C. The extrusion was not an operation as easy as in the case of the H-ZSM-5 pellets prepared for the MTG tests. The major problem encountered was the formation in the extruder, of a relatively dry cake, too hard to be extruded. This residual cake had to be humidified again to recover its plasticity. In addition, the wet pellets had a tendency to stick together. Finally, following the quick drying operation at 110°C, the pellets were calcined at 350°C for 2 hours.

2) Characterization.

X-ray diffraction spectra of the three ZnO-Cr_2O_3 samples prepared according to the co-precipitation method were taken after different pretreatments. Those spectra have been reproduced in Figures 4 to 6. A XRD spectrum of the commercial Harshaw catalyst 0312T (73% ZnO-21% Cr_2O_3-0.8% Carbon (Zn/Cr = 76/24)) as received is shown as well in Figure 7. The identification of the phases from the XRD spectra is summarized in Table 2.

As reported in Table 2, the coprecipitated samples (dried at 110°C) do not display any crystalline pattern under XRD, except the sample with the highest Zinc content (75/25 Zn/Cr atomic ratio). This indicates a highly dispersed crystalline or an amorphous state of these samples. Upon calcination, the XRD peaks of the Zinc chromite phase were clearly observed. Chromium oxide has been detected only in the sample with an excess of Chromium (Zn/Cr = 25/75) relatively to the stoechiometric spinel phase $ZnCr_2O_4$ (Zn/Cr = 33/66). It can be assumed, however, that, in this sample, most, if not all, of the Zinc is combined with Chromium into the spinel phase.

Zn/Cr	Dry 110°C	Calcined 350°C	Calcined 450°C	Calcined 600°C	Calcined 350°C + Reduced 300°C
25/75	Amorphous or highly dispersed crystalline phases	Amorphous or highly dispersed crystalline phases + Cr_2O_3 (minor phase)	-	Cr_2O_3 + $ZnCr_2O_4$	Cr_2O_3 + $ZnCr_2O_4$ (minor phase)
50/50	"	-	$ZnCr_2O_4$ + ZnO (minor phase)	$ZnCr_2O_4$ (crystal size ↑) + ZnO	-
75/25	ZnO	-	ZnO + $ZnCr_2O_4$ (relatively well dispersed phase)	ZnO + $ZnCr_2O_4$ (crystal (size ↑)	-
Harshaw Catalyst (as received 76/24)	ZnO + $ZnCr_2O_4$ (dispersed phase)	-	-	-	-
25/75 commercial method	-	-	Calcined 400°C $ZnCr_2O_4$ + Cr oxides	Calcined 555°C $ZnCr_2O_4$ + Cr_2O_3	

Table 2: XRD Characterization of the ZnO-Cr_2O_3 Samples Prepared.

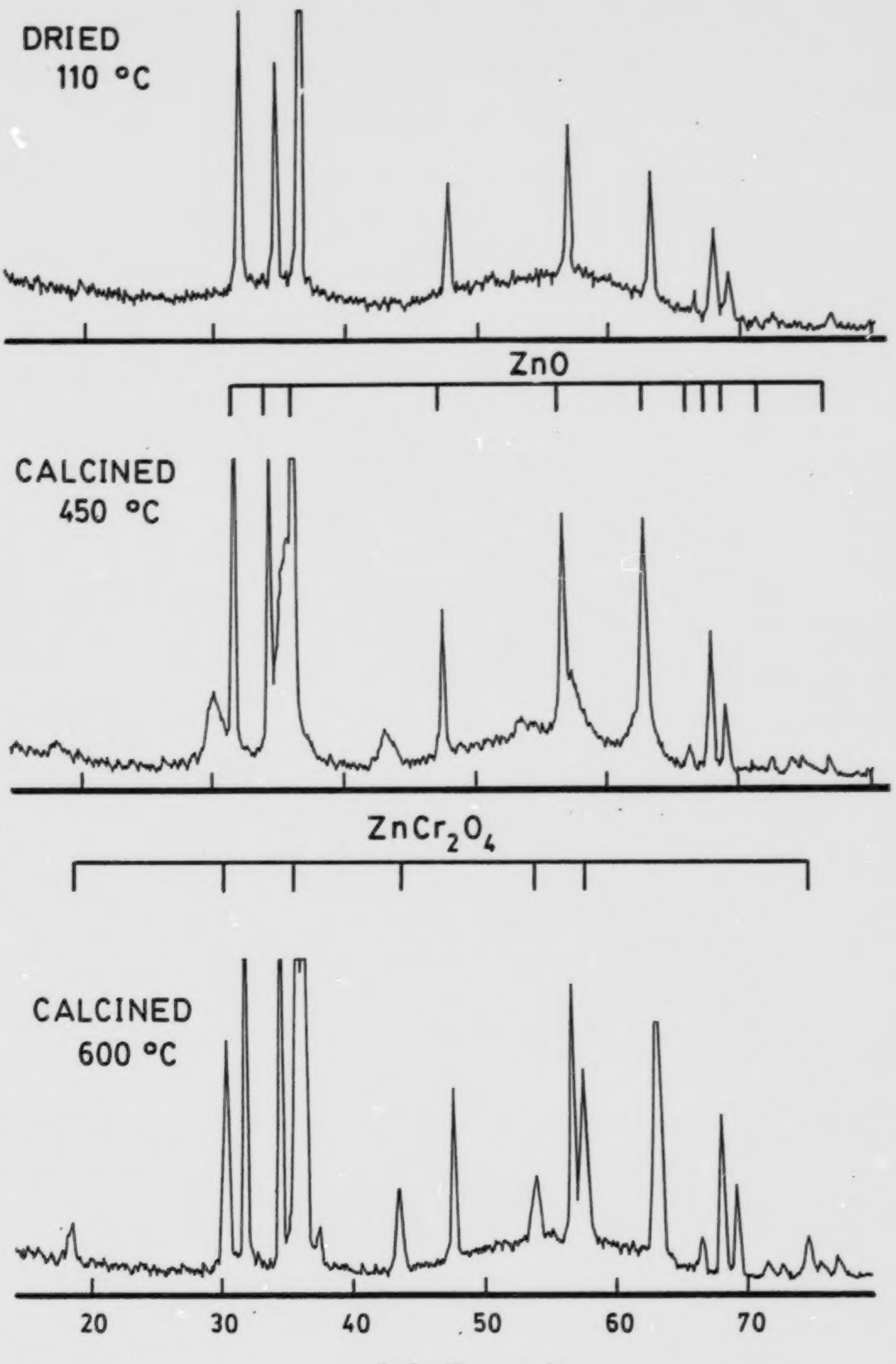


Figure 4: X-Ray Diffraction Spectra of ZnO-Cr$_2$O$_3$ Sample (co-precipitation method) with a 25/75 Zn/Cr atomic ratio.

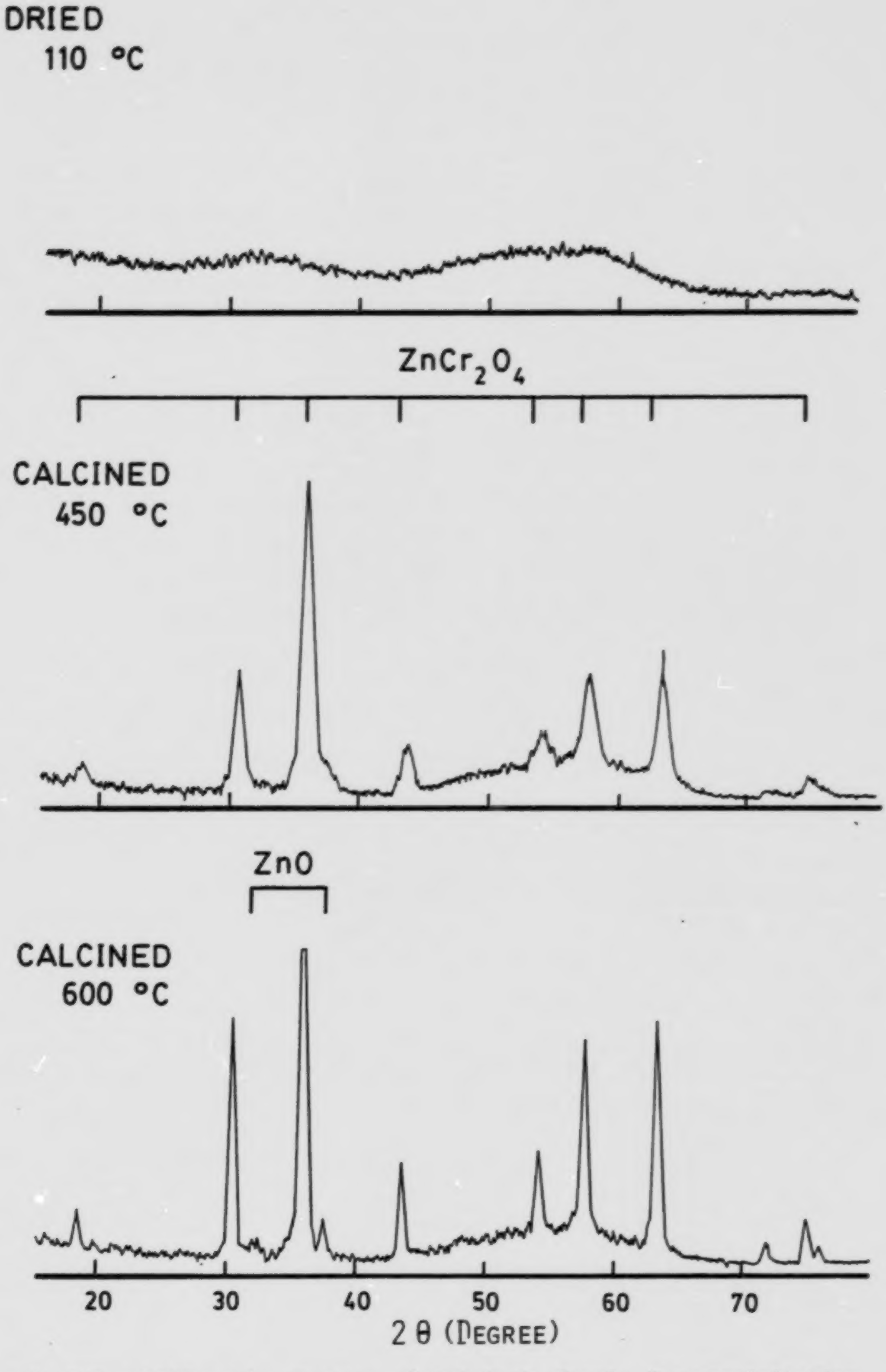


Figure 5: X-Ray Diffraction Spectra of $ZnO-Cr_2O_3$ Sample (co-precipitation method) with a 50/50 Zn/Cr atomic ratio.

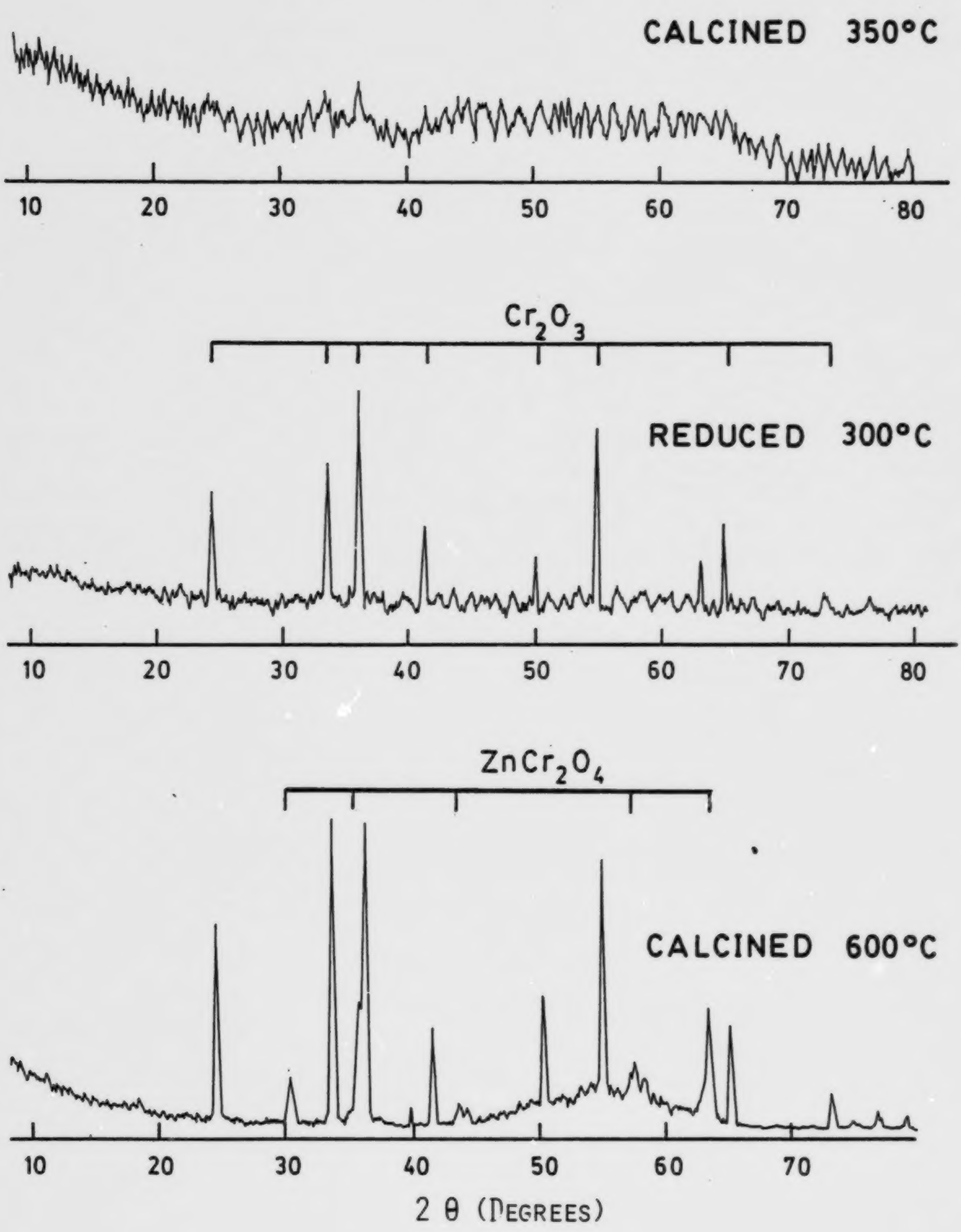


Figure 6: X-Ray Diffraction Spectra of $ZnO-Cr_2O_3$ Sample (co-precipitation method) with a 25/75 Zn/Cr atomic ratio.

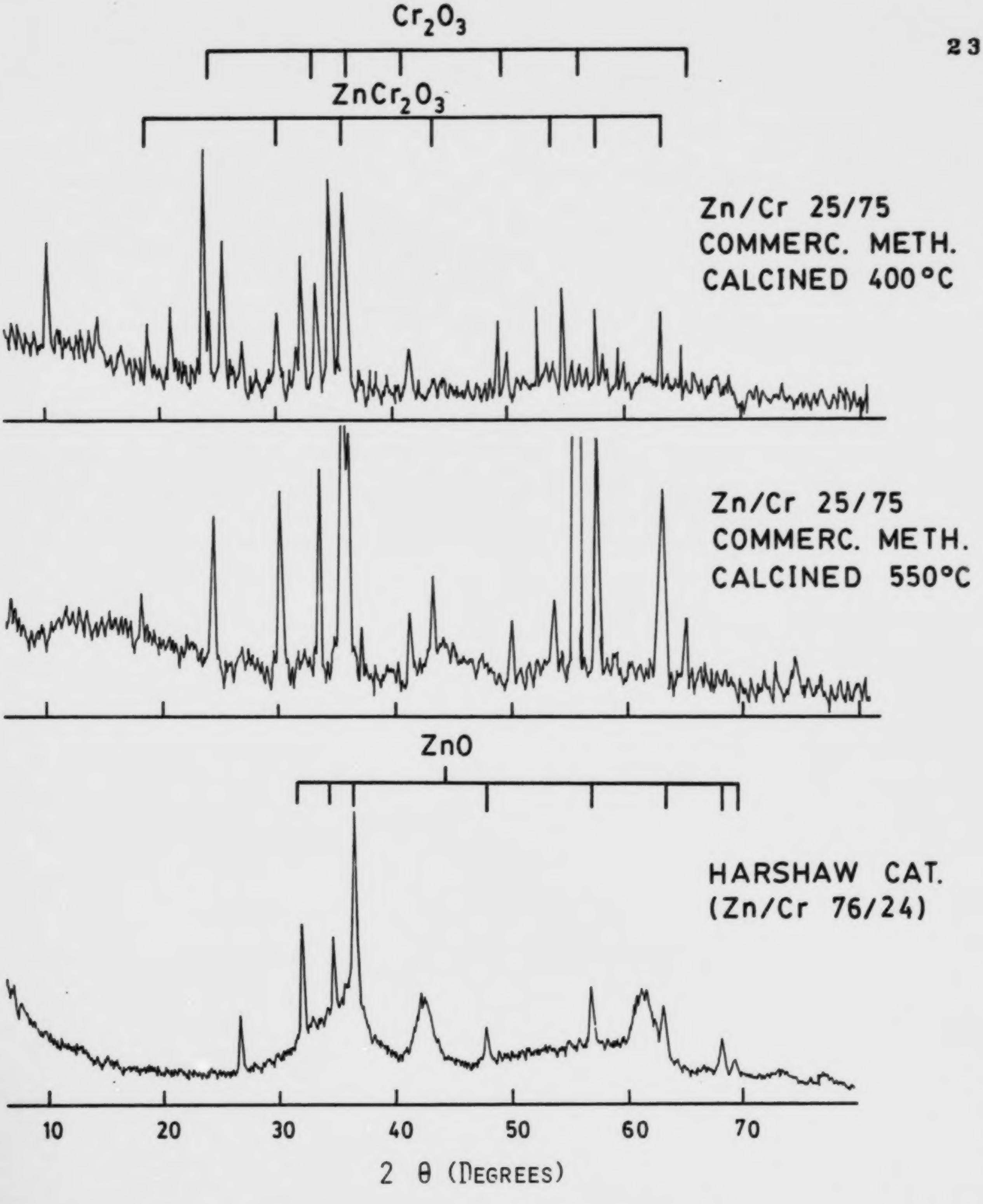


Figure 7: X-Ray Diffraction Spectra of the Harshaw ZnO-Cr$_2$O$_3$ Catalyst, and the ZnO-Cr$_2$O$_3$ Sample (impregnation of ZnO powder with chromic acid) with a 25/75 Zn/Cr Atomic Ratio.

While $ZnCr_2O_4$ is the most abundant phase in the sample with a 50/50 Zn/Cr ratio, ZnO becomes predominent in the sample with a 75/25 Zn/Cr ratio, due to the increasing excess of Zinc relatively to Chromium needed to form the spinel phase $ZnCr_2O_4$.

An increase of the calcination temperature from 450°C to 600°C is accompanied by a growth of the crystal size for each oxide form, as indicated by the narrower XRD peaks.

The sample with a 25/75 Zn/Cr ratio, calcined at 350°C, is mainly XRD amorphous with minor amounts of Cr_2O_3 detected. However, after reduction under H_2 diluted in He at 300°C, the sample displays sharp and intense peaks belonging to the Cr_2O_3 oxide phase. Weak peaks ascribed to the $ZnCr_2O_4$ phase appear too.

The XRD spectrum of the Harshaw commercial catalyst reveals the presence of ZnO and $ZnCr_2O_4$ phases, the last one being in a highly dispersed state.

The XRD spectra of the 25/75 Zn/Cr sample prepared according to the commercial method are shown in Figure 7. The major phase is Zinc chromite, $ZnCr_2O_4$, in the sample calcined at 400°C. XRD peaks, characteristic of Cr_2O_3, were detected also, besides other peaks attributed to intermediate oxide states between Cr_2O_3 and CrO_3. In accordance with the literature (Pascal 1959b), when the catalyst sample is further calcined to 550°C, complete transformation to the oxide phase Cr_2O_3 is observed, concurrently with a growth of the $ZnCr_2O_4$ spinel phase.

BET surface area measurements were conducted in a Perkin-Elmer sorptometer model 212C, using the continuous flow method. The principle of the method consists into measuring the amount of nitrogen adsorbed from known mixtures of N_2 in inert He gas flowing over the sample maintained at liquid nitrogen temperature. The amount of N_2 adsorbed at a given partial pressure of N_2 in He, is monitored with a thermal conductivity detector (TCD). The measurements were done on $ZnO\text{-}Cr_2O_3$ samples prepared by co-precipitation, with different Zn/Cr atomic ratio and submitted to various thermal treatments. The results are gathered in Table 3.

At first, three $ZnO\text{-}Cr_2O_3$ samples with 25/75, 50/50 and 75/25 Zn/Cr ratio, calcined at 350°C for four hours, were prereduced at 300°C in-situ in the sorptometer apparatus. The prereduction procedure used for the syngas conversion kinetic study was reproduced as close as possible. The sample was heated slowly to 300°C and maintained at this temperature for 16 hours in a stream of 7.8% H_2 in He. Then, the sample was cooled to room temperature before beginning the BET surface area measurement. The H_2 consumption during the reducing step was followed by recording the TCD signal. It was observed that, in all cases, the reduction began at around 200°C and was completed at 280°C.

As reported in Table 3, the surface area of the reduced $ZnO\text{-}Cr_2O_3$ samples increases with the chromium oxide content, from 56 m^2/g for the sample with the highest zinc content (Zn/Cr = 75/25) to 103 m^2/g for the sample with the lowest Zinc content (Zn/Cr = 25/75). This observation is consistent with the well established fact that the main role of chromium oxide is to increase the dispersion of zinc oxide, the active component, and to maintain a high dispersion state when the sample is brought to high reaction temperatures (Natta,1955).

Sample Zn/Cr atomic ratio	Pretreatment	BET Surface Area m^2/g
75/25	Calcined 350°C, 4 hrs + reduced 300°C 7.8% H_2 in He, 16 hrs	56
50/50	"	94
25/75	"	103
25/75	Calcined 350°C, 4hrs	87
25/75	Calcined 350°C, 4hrs + He, 400°C, 16hrs	35
25/75	Calcined 350°C, 4hrs + He, 400°C, 16hrs + H_2/CO 1/1, 400°C, 1hr	30

Table 3: BET Surface Area of the ZnO-Cr_2O_3 Samples Prepared by Co-Precipitation.

In a second series of measurements, the 25/75 Zn/Cr calcined sample was submitted to various thermal treatments. When the calcined sample was reduced at 300°C under a diluted H_2 stream, an increase of the surface area from 87 to 103 m^2/g was observed. On the contrary, a high temperature treatment (400°C) in an inert Helium atmosphere of the calcined sample resulted in a dramatic decrease of the surface area from 87 to 35 m^2/g. The sample was then reduced by quickly switching from the helium to a 1/1 molar H_2/CO mixture stream, at 400°C. In this case, the reduction occured in a few minutes, according to the TCD signal. The surface area was further decreased to 30 m^2/g.

It results from those observations that the $ZnO\text{-}Cr_2O_3$ samples are quite affected by thermal treatments. A mild and controlled pretreatment such as the prereduction at 300°C in diluted H_2 may lead to a more dispersed state of the catalyst, and, as a consequence, a higher activity per unit mass of catalyst.

SECTION III

Reactor Experiments with the Berty Reactor

- A. Methanol to Gasoline
- B. Direct Conversion of Synthesis Gas via the Methanol Route
- C. Canmet Catalysts

III. Berty Reactor Experiments.

A. Methanol to Gasoline (MTG) Conversion Experiments.

1) **Experimental Set-up.**

Runs were carried out in an Autoclave Engineer Berty recirculation reactor 3" I.D. The original basket volume was reduced to a 1" diameter - 2" hight basket by means of an aluminum insert, in order to accomodate small samples of catalyst. Methanol (purity 99.8 %) was fed with a Gilson HPLC type pump, model 402, through a vaporizer. Subatmospheric inlet partial pressures of methanol were achieved by diluting it with a stream of nitrogen. Liquid products were condensed with a water-cooled condenser. Flow rates of the non-condensed products were monitored with a bubble flowmeter.

2) **Analysis of Products.**

Composition of liquid and gaseous hydrocarbon fractions were assessed with a Hewlett-Packard (HP) model 5890 gas chromatograph, equipped with a Durabond (DB-1) 30 meter long capillary column and a flame ionization detector linked to a HP 3393A integrator. The use of a cryogenic unit provided a good separation of C_1-C_4 hydrocarbons and dimethylether. Peaks were identified with a HP 5990A mass selective detector. Methanol and water contents in aqueous fractions were measured with a HP 5730A gas chromatograph linked to a HP 3390a integrator. Methanol and water were separated on a 6 ft long- 1/8" OD Porapak column and analysed on a Thermal Conductivity Detector.

3) Run Conditions.

Runs were conducted with (25% H-ZSM-5 + 30 % Al_2O_3 binder + 45% fused Al_2O_3 diluent) 1/8" pellets. The catalyst preparation and characterization are described in the previous chapter of this report (section I-C).

Temperature and pressure range investigated covered the operating conditions considered for the Pseudoadiabatic regime, i.e. :

- temperatures from 300°C to 376°C,
- inlet partial pressures of methanol from 0.3 to 1 atm,
- WHSV from 0.45 to 1.8 g methanol $(g.catalyst.hr)^{-1}$.

By operating the Berty reactor with an impeller rotation speed of 2000 rpm and keeping the total inlet flow rate under 500 ml/min, mass transfer limitations are not expected to occur, according to previous experiments carried on with naphtalene pellets (Mahay, 1987).

The same catalyst batch (10 to 11g) was used for a series of runs, usually at the same temperature. Runs were repeated periodically in order to evaluate the degree of deactivaton of the catalyst. When not in operation, the reacting system was kept under nitrogen flow. Once new operation conditions were set, the reacting system was left stabilizing to a new steady-state for a period of 30 to 60 minutes before starting data and sample collection. Depending on the flow rate of methanol fed, the liquid sample for each run was collected over a 0.5 to 2 hours period. Gaseous samples were analyzed each 20 to 30 minutes. The liquid and gaseous fraction analysis were combined for the mass balance calculations. Given the fact that the catalyst deactivates with time on stream, the calculated compositions of the reaction products were representative of an average activity of the catalyst batch during the run.

4) Results.

Twenty-seven (27) runs were conducted. Operating conditions and product distribution are given in tables 4a to 4d. One hundred thirty two (132) compounds were identified. Total, carbon and oxygen mass balances were within 10%. Calculations were done on a HP 1000 minicomputer using a FORTRAN program. A listing of the computer program is given in appendix B, as well as a printout for one of the runs.

Methanol reaction rates were calculated from the simple CSTR mass balance:

$$r = (F_{in} \cdot y_{M,in} - F_{out} \cdot y_{M,out}) / W$$

where :

- F_{in} and F_{out} are the molar flow rates (mole/sec) at the inlet and outlet of the reactor,
- $y_{M,in}$ and $y_{M,out}$ are the molar concentrations of methanol at the inlet and outlet of the reactor,
- W is the catalyst weight (grams).

The variations of the methanol reaction rate for runs performed under the same operating conditions and with the same catalyst sample, with cumulative mass

RUN #	1a	1b	1c	12a	12b	5
OPERATING CONDITIONS						
Temperature (°C)	301.50	301.00	301.00	302.00	303.00	303.00
Outlet Methanol Pressure, (atm.)	0.137	0.158	0.162	0.190	0.185	0.254
Methanol Flowrate (mmole/min)	2.50	2.50	2.50	2.50	2.50	5.00
Inert Flowrate (mmole/min)	0.00	0.00	0.00	0.00	0.00	0.00
Test Duration (min)	114.00	117.00	118.00	126.00	118.00	83.00
Cum. Mass of Hydrocarbons (g)	2.70	5.10	7.40	31.10	32.80	35.00
PRODUCT MASS DISTRIBUTION (wt%)						
Liquid Hydrocarbons	7.4	8.8	6.8	3.3	2.8	0.7
Gaseous Hydrocarbons	20.1	17.6	15.9	14.6	13.8	9.4
Dimethylether	8.1	14.7	16.4	28.3	31.0	41.4
Water	48.9	42.4	43.6	35.3	34.5	26.8
Methanol	15.2	16.5	17.3	18.5	17.9	21.7
TOTAL HYDROCARBON MASS DISTRIBUTION (WT%)						
Methane	0.7	0.8	0.8	0.0	0.4	0.0
Ethylene	24.4	25.1	26.6	14.6	14.3	12.3
Ethane	0.0	0.0	0.0	0.0	0.0	0.0
Propylene	12.2	14.5	14.6	10.9	10.9	11.9
Propane	6.8	3.6	5.8	4.1	2.8	2.5
i-Butane	7.4	5.1	5.6	3.9	3.2	2.1
n-Butane	2.4	1.7	1.8	1.2	1.1	0.6
Butenes	4.1	3.8	4.1	5.0	4.9	4.3
Saturated C_5-C_{10}	21.1	21.1	18.2	32.6	34.7	26.7
Unsaturated C_5-C_{10}	2.9	3.4	3.1	2.6	3.3	2.8
Aromatic C_6-C_{10}	17.5	20.4	18.9	24.6	24.0	36.6
C_{11}^+	0.5	0.5	0.5	0.5	0.4	0.2

Table 4a: Results of the MTG kinetic runs in the Berty Reactor.
(Catalyst: 25% ZSM-5, 30% Al_2O_3 binder, 45% Al_2O_3 diluent)

Run #	6a	7	8	6b	6c	9	10	11	6d
OPERATING CONDITIONS									
Temperature (°C)	316.00	317.00	316.50	316.00	315.50	316.00	316.00	317.00	315.50
Outlet MeOH Pressure (atm.)	0.091	0.178	0.289	0.119	0.119	0.098	0.062	0.116	0.134
Methanol Flowrate (mmole/min)	2.50	5.00	10.00	2.50	2.50	2.50	2.50	2.50	2.50
Inert Flowrate (mmole/min)	0.00	0.00	0.00	0.00	0.00	2.40	5.00	5.00	0.00
Test Duration (min)	111.00	87.00	71.00	136.00	87.00	135.00	118.00	99.00	63.00
Cum. Mass of Hydrocarbons (g)	3.70	9.40	17.90	22.30	25.80	31.10	35.10	41.60	46.20
PRODUCT MASS DISTRIBUTION (wt%)									
Liquid Hydrocarbons	13.4	9.0	3.6	12.6	14.5	6.7	5.2	3.4	14.9
Gaseous Hydrocarbons	22.7	23.2	18.2	25.3	19.9	25.9	30.2	23.5	18.9
Dimethylether	2.6	9.4	22.0	3.0	5.3	8.6	8.7	21.0	5.0
Water	51.8	41.8	32.7	47.3	48.2	42.8	41.4	34.8	47.3
Methanol	9.5	16.6	23.5	11.8	12.1	16.0	14.5	17.3	13.9
TOTAL HYDROCARBON MASS DISTRIBUTION (WT%)									
Methane	0.3	0.3	0.4	0.3	0.3	0.3	0.4	0.4	0.3
Ethylene	10.0	12.8	14.7	9.8	11.7	14.1	16.0	17.9	11.2
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Propylene	4.6	7.3	12.9	7.7	6.1	5.7	11.9	14.9	8.3
Propane	5.9	4.4	1.3	1.9	4.8	6.4	1.7	1.0	2.2
i-Butane	8.2	6.1	3.5	7.0	6.4	6.3	7.5	5.0	6.1
n-Butane	2.4	1.7	1.2	2.2	2.0	1.5	1.4	1.1	1.8
Butenes	3.6	5.2	6.0	4.0	4.4	5.2	5.1	6.3	3.3
Saturated C_5-C_{10}	33.9	35.1	34.1	38.8	30.3	31.3	29.8	28.0	26.0
Unsaturated C_5-C_{10}	6.0	7.6	6.8	6.4	6.0	6.9	6.4	6.3	4.5
Aromatic C_6-C_{10}	24.6	19.1	18.8	21.6	27.5	21.9	19.5	18.8	35.8
C_{11}^+	0.5	0.4	0.3	0.3	0.5	0.4	0.3	0.3	0.5

Table 4b: Results of the MTG kinetic runs in the Berty Reactor.
(Catalyst: 25% ZSM-5, 30% Al_2O_3 binder, 45% Al_2O_3 diluent)

RUN #	2a	2b	2c	16a	17	18	16b
OPERATING CONDITIONS							
Temperature (°C)	337.50	338.00	338.50	338.00	337.00	337.00	337.00
Outlet MeOH Pressure (atm.)	0.050	0.060	0.064	0.084	0.061	0.044	0.100
Methanol Flowrate (mmole/min)	2.50	2.50	2.50	2.50	2.50	2.50	2.50
Inert Flowrate (mmole/min)	0.00	0.00	0.00	0.00	2.40	5.20	0.00
Test Duration (min)	118.00	126.00	127.00	126.00	118.00	142.00	126.00
Cum. Mass of Hydrocarbons (g)	4.40	8.30	12.30	23.20	34.90	38.90	44.00
PRODUCT MASS DISTRIBUTION (wt%)							
Liquid Hydrocarbons	15.6	14.4	15.6	14.0	8.0	5.6	15.8
Gaseous Hydrocarbons	25.5	23.3	22.8	20.5	30.2	31.0	17.6
Dimethylether	0.0	1.1	0.9	3.9	4.2	9.4	5.0
Water	53.6	54.6	53.7	51.3	45.8	41.6	49.4
Methanol	5.3	6.6	7.0	10.3	11.8	12.4	12.2
TOTAL HYDROCARBON MASS DISTRIBUTION (WT%)							
Methane	0.4	0.6	0.6	0.6	0.6	0.8	0.6
Ethylene	7.1	11.7	11.1	14.9	16.0	20.6	14.7
Ethane	0.1	0.1	0.1	0.1	0.0	0.0	0.0
Propylene	2.4	5.5	5.1	7.7	9.2	13.8	8.3
Propane	8.6	8.6	8.4	6.0	4.6	4.6	5.0
i-Butane	10.0	11.7	11.5	10.9	10.3	12.5	9.4
n-Butane	3.1	3.2	3.1	2.2	1.6	1.5	1.8
Butenes	2.1	3.6	3.3	3.7	4.5	4.7	3.8
Saturated C_5-C_{10}	27.9	25.2	24.0	23.5	23.2	19.6	24.6
Unsaturated C_5-C_{10}	3.3	3.6	3.4	2.9	4.8	3.2	4.2
Aromatic C_6-C_{10}	34.4	25.7	28.9	27.1	24.8	18.3	27.1
C_{11}^+	0.6	0.5	0.5	0.4	0.4	0.4	0.5

Table 4c: Results of the MTG kinetic runs in the Berty Reactor.
(Catalyst: 25% ZSM-5, 30% Al_2O_3 binder, 45% Al_2O_3 diluent)

RUN #	3a	3b	4	13	14	15
OPERATING CONDITIONS						
Temperature (°C)	347.50	347.00	349.50	364.00	369.00	377.00
Outlet MeOH Pressure (atm.)	0.074	0.064	0.112	0.050	0.090	0.158
Methanol Flowrate (mmole/min)	2.50	2.50	5.00	2.50	5.00	10.00
Inert Flowrate (mmole/min)	0.00	0.00	0.00	0.00	0.00	0.00
Test Duration (min)	119.00	133.00	99.00	126.00	83.00	62.00
Cum. Mass Hydrocarbons (g)	18.00	21.50	26.00	3.80	10.20	19.60
PRODUCT MASS DISTRIBUTION (wt%)						
Liquid Hydrocarbons	15.2	15.4	12.8	14.9	13.7	10.9
Gaseous Hydrocarbons	21.8	23.3	23.8	23.3	23.5	23.2
Dimethylether	1.2	1.0	2.6	0.1	1.0	2.8
Water	54.1	53.4	49.6	56.1	51.9	46.6
Methanol	7.7	6.9	11.2	5.6	9.9	16.5
TOTAL HYDROCARBON MASS DISTRIBUTION (WT%)						
Methane	0.6	0.6	0.6	0.9	0.9	1.0
Ethylene	11.6	11.3	13.9	9.6	14.0	18.0
Ethane	0.0	0.1	0.0	0.3	0.2	0.1
Propylene	5.2	5.1	6.8	4.5	7.4	10.8
Propane	7.4	7.3	6.2	11.2	7.6	5.9
i-Butane	11.9	12.3	11.2	16.1	14.1	12.2
n-Butane	2.4	2.5	2.2	3.5	2.4	1.8
Butenes	2.9	2.8	3.8	2.3	3.4	4.4
Saturated C_5-C_{10}	24.5	24.7	26.8	18.8	20.3	19.7
Unsaturated C_5-C_{10}	5.8	3.2	4.7	2.6	3.7	4.2
Aromatic C_6-C_{10}	27.2	29.6	23.3	29.3	25.4	21.4
C_{11}^+	0.5	0.5	0.5	0.9	0.6	0.5

Table 4d: Results of the MTG kinetic runs in the Berty Reactor.
(Catalyst: 25% ZSM-5, 30% Al_2O_3 binder, 45% Al_2O_3 diluent)

of hydrocarbon produced per mass of catalyst at each reaction temperatures studied, are given in Figure 8. This figure shows that an initial fast activity decay is followed by a slower deactivation. It can be observed from the same figure that the degree of deactivation increases with the reaction temperature. Coke formation being the main factor of catalyst deactivation, it was considered more appropriate to correlate the deactivation rate with the formation of the coke precursors, i.e. hydrocarbons formed, rather than with such variables as the cumulative time-on-stream or the cumulative mass of methanol fed. The use of this variable would have been justified only if operating conditions, especially WHSV, were kept constant.

5) Kinetic Studies.

In a first attempt, the methanol conversion rates, r, measured between 301 and 347°C, were fitted with a first order kinetic, including an exponential deactivation term:

$$r = k_0 \cdot e^{-E/RT} \cdot e^{-\alpha\,(mHC/W)} \cdot P_M$$

where,

- P_M is the partial pressure of methanol in the reactor (actually, the methanol partial pressure measured at the exit of the reactor),
- k_o is the preexponential factor,
- E is the activation energy,
- mHC is the cumulative mass of hydrocarbons formed per unit mass of catalyst.

Methanol conversion rates measured and calculated are compared in Figure 9. Calculated values were obtained with the following parameters:

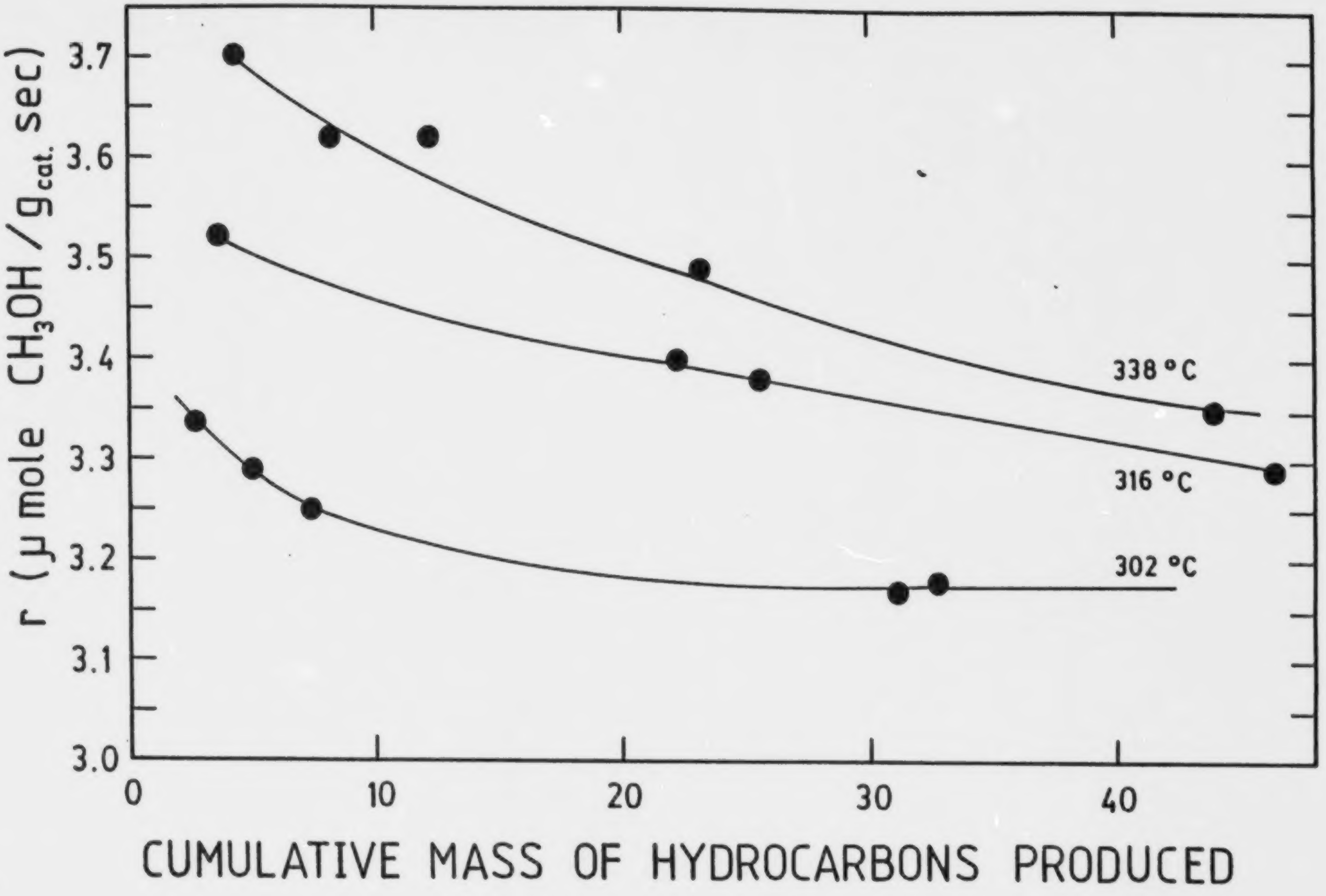


Figure 8: Change of Methanol Conversion Rate with the Cumulative Mass of Hydrocarbon Produced.

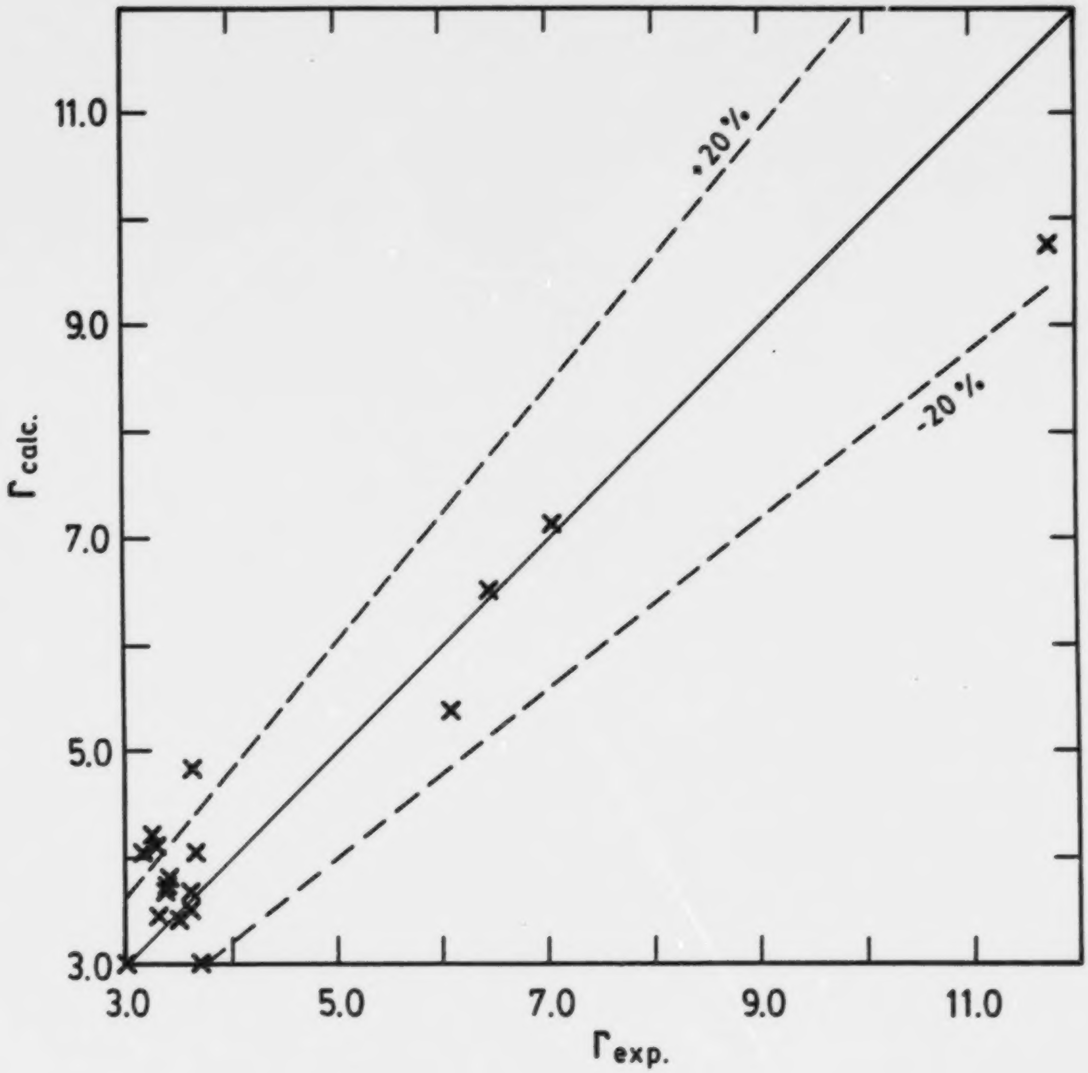


Figure 9: Comparison of Experimental Values and Calculated Methanol Conversion Rate, using a 1st Order Kinetic Equation.

$E = 15.7 \pm 3.6$ kcal/mole

$k_0 = 26$ mole.sec^{-1}.g$_{cat}{}^{-1}$.atm^{-1}

$\alpha = 8.10^{-4}$ g$_{cat}$/g$_{cum.\ HC\ produced}$.

The activation energy, E, has a value close to the one proposed by Mobil Oil researchers for the same type of ZSM-5 catalyst: 12 kcal/mole (Chang, 1983). However, this value was obtained by Mobil researchers in a higher temperature range: 345°C-480°C. Furthermore Doelle et al. (1981) have proposed a higher value, 19 kcal/mole, for a much lower temperature range, 115°C-200°C, where only dimethylether was observed.

An Arrhenius plot with the kinetic constants corrected for deactivation is shown in Figure 10. It appears that a linear variation is observed for the runs performed between 300°C and 335°C. This is particularly true if only the results obtained with the fresh catalysts are taken into account (Runs 1a, 6a, 2a). In that case, the activation energy is close to 20 kcal/mole. On the contrary, the values reported at 350°C deviates from linearity. This indicates that, at this higher temperature, where the conversion to liquid hydrocarbons becomes predominant, the simple first order kinetic model is not suitable any more to provide a good representation of the MTG reaction. Thus, it is necessary to take into account a more detailed reaction scheme.

Different models were tested in the context of the present program. One of the most interesting ones is a model proposed by Chang (1980), based on the following considerations:

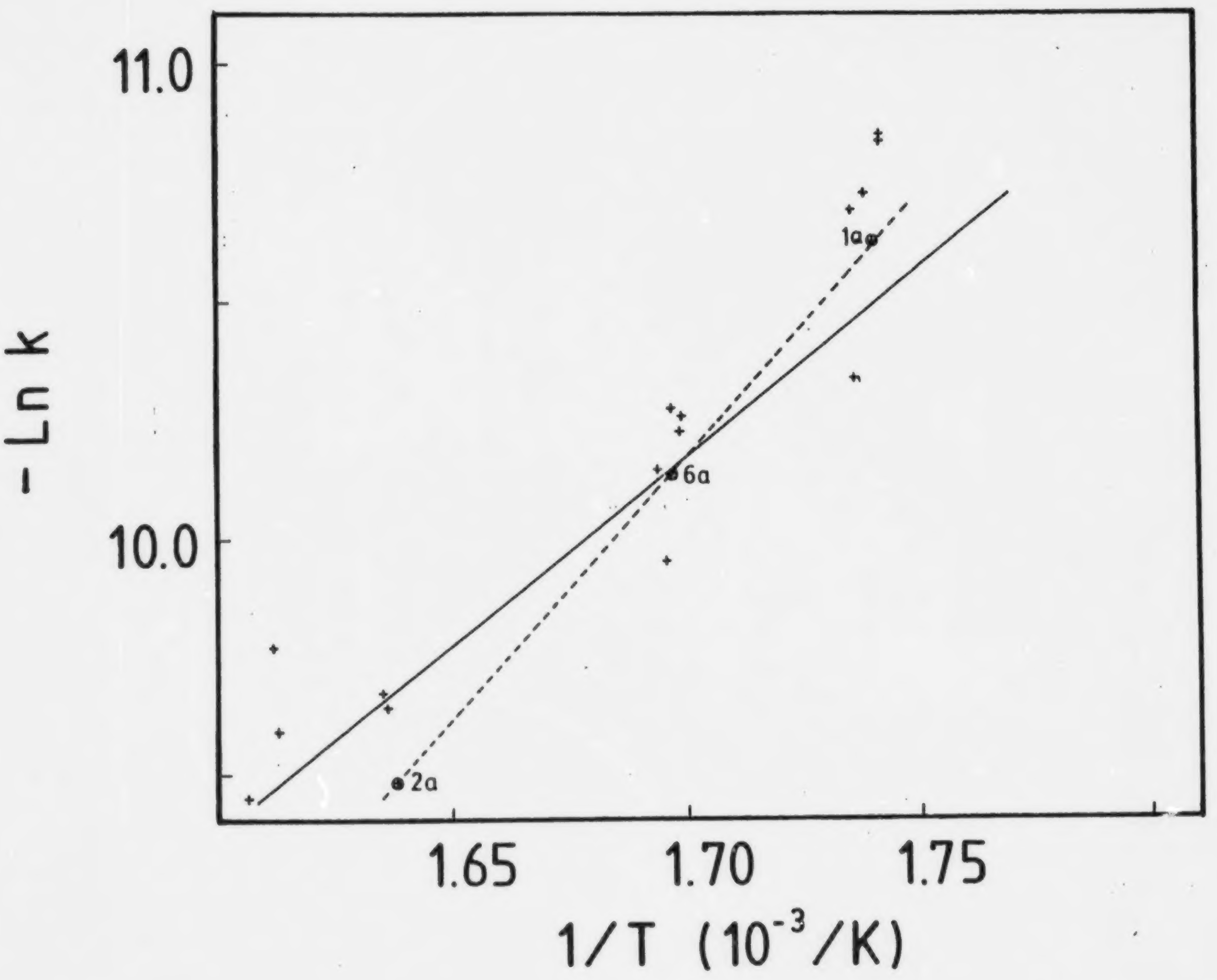


Figure 10: Arrhenius Plot for the 1st Order MTG Reaction Rate Equation. (k values are corrected for deactivation) ___ : All runs; ---- : Fresh Catalyst Only.

- the dehydration of methanol to dimethylether :

$$CH_3OH \quad = \quad CH_3OCH_3 + H_2O$$

is a fast reaction and the thermodynamic equilibrium is reached under the reaction conditions used. As a consequence, methanol and dimethylether can be lumped in a single species;

- The model takes into account the autocatalytic nature of the methanol conversion to hydrocarbons, established by several independant studies (Ono, 1981; Chen and Reagan, 1979).

- all species have the empirical formula (CH_2). This means that the lumped product distribution is expressed on a carbon basis.

Then, the reaction sequence proposed is as follows:

$$[CH_2]_{\text{oxygenates}} \xrightarrow{k_1} B$$
$$B + [CH_2]_{\text{oxygenates}} \xrightarrow{k_2} [CH_2]_{\text{light olefins}}$$
$$B + [CH_2]_{\text{light olefins}} \xrightarrow{k_3} [CH_2]_{\text{light olefins}}$$
$$[CH_2]_{\text{light olefins}} \xrightarrow{k_4} [CH_2]_{\text{aromatics+paraffins}}$$

where B is a very reactive species. Thus, by invoking the steady-state assumption on B, its rate of formation can be fixed to zero.

From this set of reaction equations, the following relations are derived:

$$dA/dt = k_1A + k_2A\,B$$
$$dB/dt = k_1A - k_2A\,B - k_3B\,C = 0$$
$$dC/dt = k_2AB + k_3BC - k_4C$$

where,

A are the oxygenated species,

B is a very reactive intermediate species,

C is the C_2-C_5 olefins lump,

D is the aromatics + paraffins lump.

This set of equation is reduced to:

$$- dC/dt = \frac{k_2 A + k_3 C}{2k_2 A + k_3 C} \quad . \; (1 - \frac{k_4}{k_1} \quad \frac{C}{A})$$

This equation is equivalent to:

$$- dU/dA = \frac{1}{A} \; (\; (\frac{1 + K_1 U}{2 + K_1 U}) \; (1 - K_2 U) + U))$$

$$U = C/A, \qquad K_1 = k_3/k_2, \qquad K_2 = k_4/k_1$$

With the following conditions at the limits:

$$A = 1, \qquad U = 0$$

The resulting differential equation is integrated to:

$$\mathrm{Ln}\, A = \frac{K_1 - 2}{\gamma} \; \mathrm{Ln} \; [\; \frac{2\alpha \, U + \beta - \gamma}{2\alpha \, U + \beta + \gamma} \quad \frac{\beta + \gamma}{\beta - \gamma} \;]$$

$$- \frac{K_1}{2 \, \alpha} \; \mathrm{Ln} \; (\; 1 + \beta U + \alpha U^2 \;)$$

with :

$$\alpha = K_1 \; (\; 1 - K_2 \;)$$

$$\beta = K_1 - K_2 + 2$$

$$\gamma = \sqrt{\beta^2 - 4\alpha}$$

One of the advantages of such a mathematical treatment of this model, is that no estimate of the deactivation effect or function is required. Nevertheless, this is valid only if the coke formation affects equally each reaction step.

The best estimates of K_1 and K_2 kinetic parameters were calculated with a non-linear regression Marquardt algorithm for each set of results at a given temperature. The objective function, in this case, was:

$$\phi = \Sigma [(\mathrm{Ln}\ A)_{calc} - (\mathrm{Ln}\ A)_{exp}]^2$$

A listing of the computer program, similar to the one proposed by Kuester and Mize (1973) is given in appendix E.

The parameter estimates, along with the observed and predicted values of A, are shown in Table 5 for the four temperatures : 301°C, 315°C, 337°C and 370°C. The calculated and experimental distributions of the lumped products have also been plotted in triangular diagrams, in Figures 11a and 11b. As shown in the figures and the table, fitting of the data is quite acceptable. However, values of K_1 and K_2 do not obey the Arrhenius law. This is believed to be due to the levels of conversion which were higher than expected, especially at 315°C and 337°C. As a consequence, those kinetic data are not discriminatory enough for the parameter estimation, using a Marquardt algorithm. Thus, few more runs are advised, covering a wider range of conversions to complete the kinetic study for the MTG reaction.

	OXYGENATED A_{EXP}	LIGHT OLEFINS OLEFINS C_{EXP}	AROMATICS AND PARAFFINS D_{EXP}	$A_{CALC.}$	ERROR% on A
301°C K_1 - 306, K_2 - 0.53					
	0.230	0.320	0.450	0.232	1.2
	0.326	0.299	0.375	0.322	1.2
	0.382	0.285	0.333	0.367	3.8
	0.747	0.073	0.180	0.716	4.1
	0.552	0.142	0.306	0.581	5.1
	0.590	0.129	0.281	0.608	3.1
315°C K_1 - 2.3, K_2 - 0.44					
	0.087	0.181	0.732	0.104	20.3
	0.091	0.214	0.695	0.090	0.1
	0.143	0.206	0.651	0.155	8.9
	0.139	0.207	0.654	0.150	8.1
	0.216	0.217	0.567	0.219	1.5
	0.447	0.195	0.358	0.410	8.2
	0.204	0.217	0.579	0.208	2.1
	0.190	0.283	0.527	0.150	21.0
	0.389	0.251	0.360	0.315	19.0
337°C K_1 - 41.1, K_2 - 0.55					
	0.050	0.211	0.739	0.049	1.0
	0.044	0.196	0.760	0.047	4.7
	0.122	0.238	0.640	0.135	10.8
	0.147	0.237	0.616	0.166	12.8
	0.115	0.274	0.611	0.107	6.6
	0.200	0.326	0.474	0.164	18.0
370°C K_1 - 3.45, K_2 - 0.40					
	0.012	0.171	0.817	0.012	1.4
	0.050	0.246	0.704	0.053	6.6
	0.105	0.308	0.587	0.100	5.0

Table 5: Estimated Parameters for the MTG Reaction Scheme using the Chang Kinetic Model.

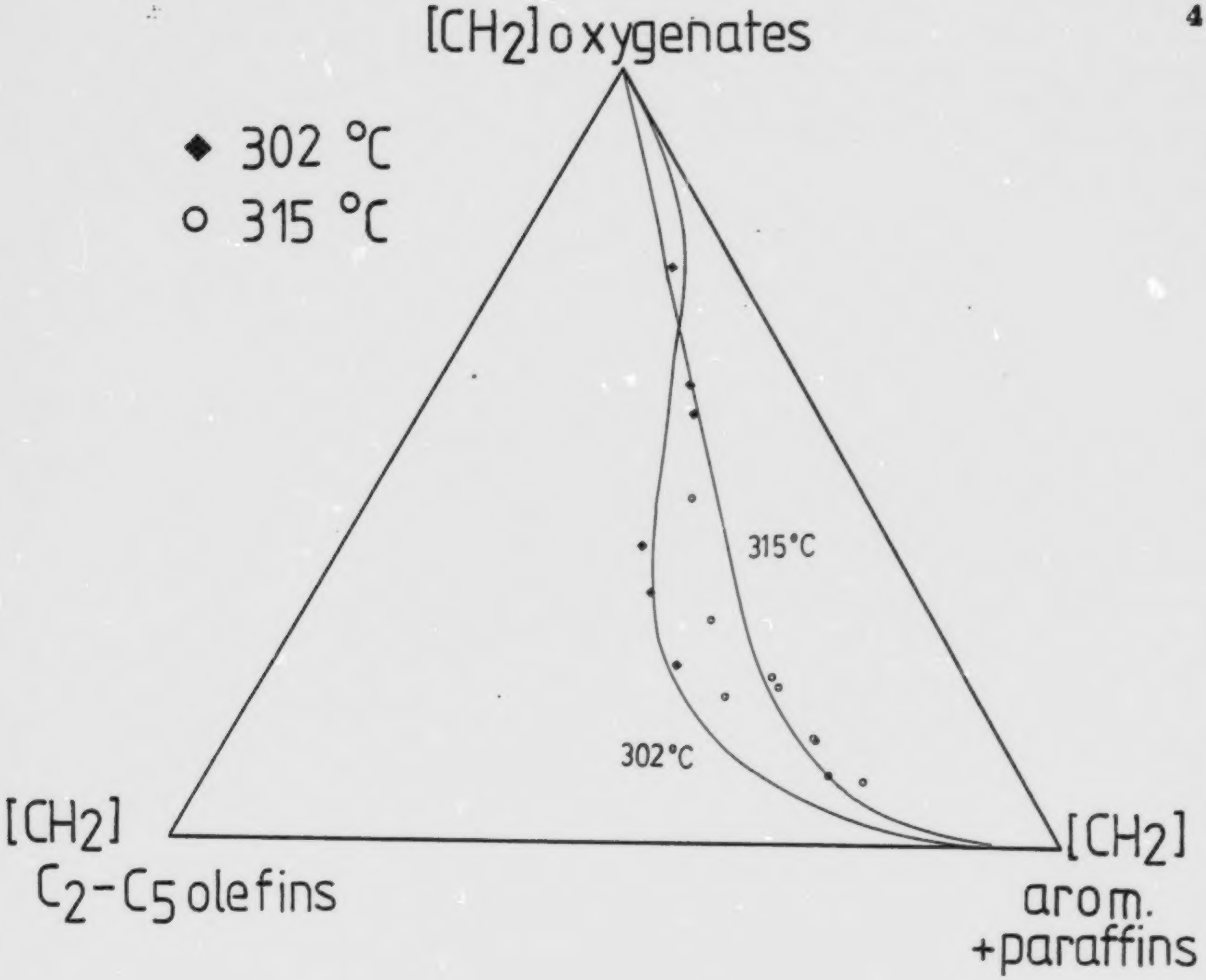


Figure 11a: Comparaison of Experimental and Calculated Product Distributions, at 302°C and 315°C, using the Chang MTG Reaction Scheme.

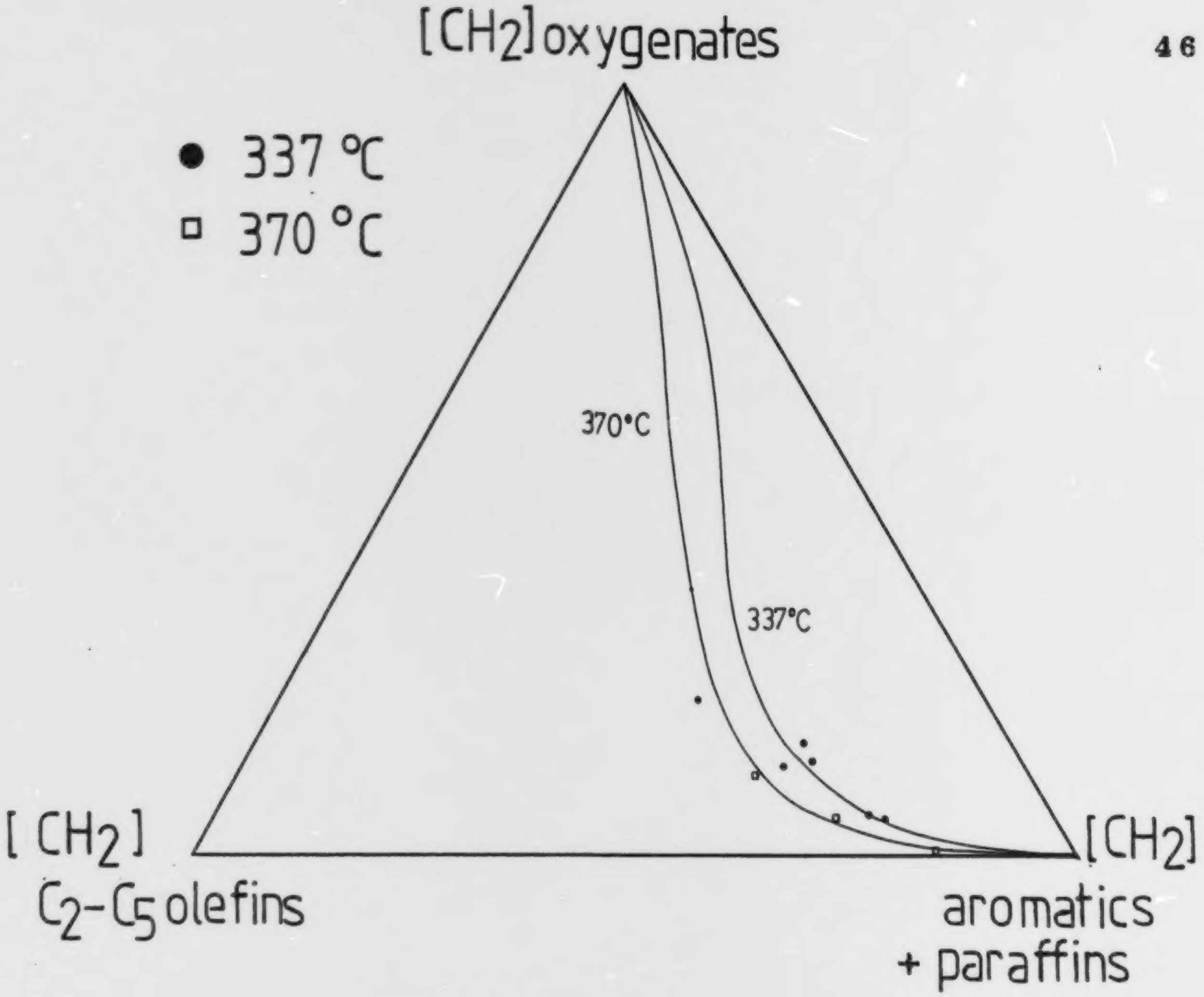


Figure 11b: Comparaison of Experimental and Calculated Product Distributions, at 337°C and 370°C, using the Chang MTG Reaction Scheme.

B. Direct Conversion of Syngas to Hydrocarbons via the Methanol Route.

1) Experimental Set-up.

The same set-up as described in the previous section was used with some modifications. A hot trap, made of 1/8" pellets of molecular sieve 13X, heated at 220°C, was installed before the reactor inlet to remove iron carbonyls from the feed composed of mixtures of H_2 and CO. An oxy-trap and a drierite trap, to eliminate traces of oxygen and water, were used as well.

The presence of a carbonyl trap became necessary when high conversions to light hydrocarbons, mainly methane, and CO_2 were observed during blank runs, performed with glass beads. Analysis of the beads revealed that iron deposition occured during the test. This is believed to be due to an unusual high content of iron carbonyls in the CO/H_2 mixture cylinder. Those carbonyls decomposed at high temperature into metallic iron, a conventional catalyst for syngas conversion and water gas shift reaction. The reactant mixture cylinder was purchased a few years ago. The assumption that the long residence time of the carbon monoxide in the carbon steel tank was the reason of this high level of iron carbonyls in the feed was confirmed when no more deposits were observed after the replacement of the old syngas mixture by a bottle of a fresh syngas mixture. The iron deposits were removed from the wall of the reactor and from the basket with sand paper and, the heated transfer lines were replaced.

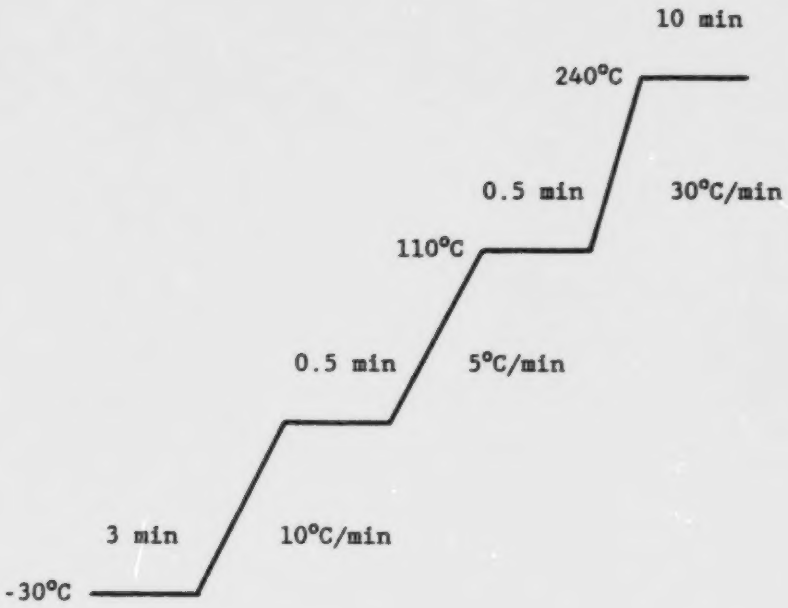
The pressure in the system was maintained at a selected value with a Tescom back pressure regulator model 26-3200, located at the reactor exit. The product stream, maintained at 250°C, was depressurized to atmospheric pressure before flowing through a heated 6 port Valco injection valve equipped with a 1 ml loop, for on-line GC analysis. Liquid samples were collected in a trap immersed in a water-ice bath. The flow rate of the non-condensed products was measured with a bubble flowmeter. Finally, the stream was sent outside the building through a ventilated exhaust.

2) Product Analysis.

As mentioned in the previous section, the hot stream leaving the reactor was analysed on-line by gas chromatography using a HP gas chromatograph model 5890 equipped with a cryogenic unit.

Products could be analysed with a Porapak Q 6ft-1/8" packed column and a TCD detector. The column was initially maintained at -10°C for 1 minute, for the separation of H_2 and CO, then was heated at 40°C/min up to 240°C. Then, H_2, CO, CO_2, H_2O and oxygenated compounds in the product stream were determined with this analysis.

The content of the 1ml loop could also be injected into a 25m-.33um HP-1 crossed-linked methyl-silicone capillary column linked to a FID detector. The temperature program was the following :



This analysis gave the total hydrocarbon product distribution. The composition of the hydrocarbon liquid fraction and, of the hydrocarbon fraction in the gaseous stream after the cold trap were determined also, using the same capillary column and temperature program.

3) Data Processing.

In a first step, the results of the analysis on the packed column were processed with a computer program called TCDPRO, to make a first estimate of the H_2 and CO conversions and, of the product distribution. The conversions were calculated by comparing the H_2 and CO determinations in the reactant and product streams, according to the following equation :

$$\text{conv.} = \frac{Q_{out} \cdot PA_{product}}{Q_{in} \cdot PA_{feed}} \cdot C$$

where, Q_{in} and Q_{out} are the volumetric flow rates of the inlet and outlet streams, $PA_{product}$ and PA_{feed} are TCD peak area for H_2 and CO, from the analysis of respectively the outlet and inlet stream. C is a correction factor which takes into account the variations of the loop temperature and, of the pressure drop through the loop, those two parameters affecting the amount of sample injected.

Mass balances were also established by comparing the mass per unit time of feed converted, calculated from the conversions, with the mass per unit time of products, calculated from the analysis of the loop content. The volume of the loop was back-calculated from the analysis of the feed and of the product streams to be compared to the expected value of 1000 μl. Those two calculations, the mass balance and the loop volume, were used to evaluate the validity of the analysis and, of the method used.

In a second step, the overall molar composition of the stream exiting the reactor, including H_2, CO, CO_2, the individual oxygenated and hydrocarbon compounds, were determined and were used for the kinetic modelling of the reactor. This was achieved with the computer program called SGPROD in the following manner.

First, the hydrocarbon distribution calculated from the analysis of the products on the packed column was erroneous due to the fact that this column is not suitable for the determination of the C_5^+ compounds in low concentration with a good accuracy. Actually, the total hydrocarbon distribution was obtained from the analysis on the capillary column. To establish the true value of the hydrocarbon weight fraction in the products, the value given by the analysis on the packed column was corrected by comparing the individual weight fractions of CH_4, C_2 and C_3 hydrocarbons in the truncated hydrocarbon distribution, determined from the analysis on the packed column, with their respective values in the total hydrocarbon distribution.

Then, the total outlet flow rate was assessed by adding to the measured flow rate of the non-condensed products the contribution of the condensed fraction. It has to be pointed out, however, that this correction was a minor factor, representing less that 0.5% of the total flow rate in most cases.

Finally, the overall molar composition of the stream at the reactor outlet was established. From the feed and product compositions, H_2 and CO conversions, total, carbon and oxygen mass balances were calculated.

Listings of the main program, SGPROD and, of the subroutines TCDPRO and TCDDAT can be found in appendix D. A copy of the printout for one of the kinetic runs is also reported.

4) Preliminary Experiments.

Twenty-four (24) experiments were conducted to establish the effect of:

- the atomic Zn/Cr ratio of the MSC component,
- the method of preparation of the MSC component,
- the addition of an alumina binder,
- the time on stream,

- the H_2/CO ratio (1 or 2),
- the temperature (350°C-400°C),
- the pressure (300 - 650 psig),
- the pretreatment.

The proportion of MSC and zeolite components was fixed for all the runs to the following ratio : $ZnO-Cr_2O_3$/H-ZSM-5 = 70/30 wt. When no binder was used, the catalyst samples tested were under the form of agglomerates, prepared according to the dry compression method.

A first set of runs was conducted with a 2/1 H_2/CO feed. The MSC component was either the Harshaw commercial catalyst or the $ZnO-Cr_2O_3$ catalyst prepared by co-precipitation, with a 50/50 Zn/Cr atomic ratio. Results at different operating conditions are shown in Table 6. The tests made with the Zn/Cr 50/50 component (Runs 1-4) show that an increase in residence time (Runs 2 → 1), in pressure (Run 2 → 3) or in temperature (Run 3 → 4) results in an increase of CO and H_2 conversions. However product distributions are barely changed.

The sample with the Harshaw catalyst as the MSC component, lose activity when increasing temperature (Runs 5 and 6). This loss of activity could be the result of an more important decrease of the MSC component surface area at higher temperature. Indeed, BET surface area measurements has revealed that this type of catalyst has a high tendency to sinter when exposed to high temperatures. In the meantime, a lower methane activity was observed as well as a shift to higher molecular weight hydrocarbons, as indicated by the hydrocarbon product distribution. This effect could be related to the change of morphology of the MSC component or, more simply, to an increase of the selectivity for CH_3OH

Run #	1	2	3	4	5	6
MSC Component Composition	Zn/Cr 50/50				Harshaw Commercial Catalyst	
H_2/CO	2				2	
P (psig)	410	410	640	640	640	640
T (°C)	325	325	325	352	357	405
Flow (mmole/gr.cat/min)	1.2	2.4	2.6	2.6	2.2	2.9
CO Conversion	26.3 - 26.8	17.7 - 11.4	20.8 - 16.3	27.6 - 25.4	58.4 - 37.9	24.7 - 21.7
H_2 Conversion	12.6 - 13.0	15.2 - 6.1	11.8 - 9.7	14.2 - 11.8	37.5 - 16.7	13.2 - 8.3
Product Distribution (wt%)						
CO_2	55.3 - 55.8	60.0 - 54.4	55.5 - 57.8	59.5 - 61.5	58.6 - 60.7	64.7 - 64.3
H_2O	13.8 - 13.2	18.2 - 17.0	14.7 - 13.6	10.9 - 10.2	12.0 - 9.6	9.6 - 8.2
HC	30.9 - 31.0	21.8 - 28.7	29.9 - 28.6	29.7 - 28.2	29.2 - 30.6	26.3 - 27.5
Hydrocarbon Distribution (wt%)						
CH_4	47.2 - 47.5	53.6 - 49.3	47.1 - 51.3	49.8 - 55.3	46.8 - 53.6	27.5 - 21.0
$C_2^=$	0	0	0	0	0	1.9 - 2.2
C_2	14.9 - 14.9	16.7 - 15.3	15.2 - 15.7	15.5 - 16.3	15.9 - 14.3	12.1 - 11.7
$C_3^=$	0	0	0	0	0	0
C_3	15.9 - 16.0	10.4 - 15.0	15.8 - 13.8	15.1 - 14.2	17.7 - 12.1	10.1 - 10.3
C_4's	14.6 - 14.4	9.9 - 16.0	14.4 - 15.3	12.9 - 12.5	14.1 - 11.6	18.2 - 40.1
C_5^+	7.4 - 7.2	9.4 - 1.8	7.4 - 3.0	6.7 - 1.7	5.5 - 8.5	30.2 - 14.9
MeOH	0	0	0	0	0	0

Table 6: Results of the Preliminary Syngas Conversion to Hydrocarbons Runs in the Berty Reactor.

synthesis relatively to methanation at higher temperatures.

Comparing the two different catalyst formulations, under similar conditions (Runs 4 and 5) shows that the sample containing the Harshaw catalyst is more active, as a consequence of its higher Zinc content, the active component for the syngas conversion. In the mean time, the product distributions were similar. In any of these runs, no methanol was detected, indicating a complete conversion of the methanol on the zeolitic component of the catalyst and an appropriate operation of the catalyst under the "drain-off" effect conditions.

Screening tests were conducted in order to determine the best Zn/Cr ratio for the methanol synthesis component of the catalyst. Those comparative runs were carried out with the same operating conditions: 640 psig, 405-410°C, 2.9 mmoles/gr cat/min.

The gas fed was a H_2/CO mixture with a molar ratio equal to 1. Results are gathered in Table 7.

The effect of Zn/Cr ratio was evaluated by comparing Runs 8, 9 and 10, (Table 7). The catalyst with a 50/50 Zn/Cr was used extensively in previous runs (1 to 4, Table 6) and may be deactivated. However, it was observed that the total conversion, based on CO and H_2 increase with the Zinc content of the MSC component. This is linked to the fact that the Zinc is the active component for the methanol synthesis and higher activity must be expected. At the same time, selectivity for C_5^+ fraction decreased with an increase in Zn/Cr ratio due to a higher hydrogenation, catalyzed by Zinc. As a consequence a higher fraction of the light olefins, produced as a primary intermediates from methanol on the

Run #	7	8	9	10	11
Zn/Cr atomic ratio	75/25	75/25	50/50	25/75	25/75
pretreatment	Dried + He/400°C	Calcined + He/400°C	Calcined + He/400°C + Runs 1-4 + He/400°C	Calcined + He/400°C	Used + He/400°C
H_2/CO	1	1	1	1	1
P (sig)	640	640	640	640	640
T (°C)	410	410	410	410	410
Flow (mmole/gr.cat/min)	2.7	3.2	3.0	2.7	2.9
CO Conversion	49.6-39.5	38.6-35.8	33.6-21.5	22.9-14.5	11.0-11.3
H_2 Conversion	43.7-32.6	29.9-28.3	27.8-15.3	13.4-6.9	4.7-6.6
Product Distribution (wt%)					
CO_2	67.1	67.6	69.1	70.2	66.4
H_2O	3.5	3.5	5.3	5.3	7.7
HC	29.4	28.8	25.6	24.5	25.9
CH_3OH	0	0	0	0	0
Liquid collected (g)					
HC	1.59	1.12	not measured	2.93	2.5
H_2O	1.71	0.95		0.0	0.0
Total Test Time (min)	285	320	290	360	370
Hydrocarbon Distribution (wt%)					
CH_4	22.7-18.2	10.3	8.0	6.3	4.0
$C_2^=$	0.5-0.6	0.7	0.8	1.2	2.2
C_2	11.5-10.7	7.65	6.1	4.6	6.4
$C_3^=$	0	0	0	0	0
C_3	23.6-22.5	23.9	28.8	10.4	8.5
C_4's	15.3-19.2	23.6	23.3	3.6	4.3
C_5^+	26.4-28.8	34.4	33.0	73.9	74.6
C_5^+ Distribution (wt%)					
C_5	27.9-36.3	39.4	0.0	2.4	3.6
C_6	7.8-12.1	14.1	52.6	0.6	1.6
Toluene	1.3-0.9	0.8	1.0	3.2	2.3
C_8 Aromatics	14.3-11.0	10.2	12.7	26.2	20.5
C_9 Aromatics	23.9-19.2	18.1	19.1	40.9	41.8
C_{10} Aromatics	9.5-9.1	9.1	8.2	7.7	12.5
C_{11}^+	14.3-7.3	2.7	~2.1	15.9	~15.0

Note: - First and second reported values for the conversion observed respectively at the beginning of the run and at the end of the run.

Table 7: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Zn/Cr Ratio in the MSC Component.

zeolitic component, are hydrogenated and then cannot be converted into gasoline by oligomerization and dehydrocyclization on ZSM5. Then it is understandable that the catalyst showing the highest yield for liquid hydrocarbon fraction is the sample with a Zn/Cr ratio of 25/75.

Other phenomena observed were an important catalyst deactivation, mainly at the beginning of the run (initial and final H_2 and CO conversions are indicated in the Tables of results) and a considerable water gas shift activity as most of the water produced from the methanol on H-ZSM5 was converted to CO_2.

Runs 10 and 11, performed with fresh and used samples of catalyst with a 25/75 Zn/Cr atomic ratio, showed that the activity of the catalyst reached a stable level after several hours on stream. Product distribution were virtually unchanged.

Runs 7 and 8, performed on a sample with a 75/25 Zn/Cr ratio, showed that the calcination under air at 350°C did not affect the activity of a catalyst which was dried at 110°C, kept under helium overnight at 400°C and tested under reaction conditions. Indeed, the calcined sample displays a conversion of CO and H_2 similar to that measured at the end of the previous test made with the non-calcined sample.

As a conclusion of this series of runs, samples with a 25/75 Zn/Cr atomic ratio were selected for further testing.

Runs 11 to 15 were conducted on a catalyst made of 30% HZSM-5 and 70% MSC component characterized by a Zn/Cr atomic ratio of 25/75 in order to evaluate the effects of the operating conditions. Results are reported in Table 8.

Temperature was the major factor influencing the conversion as shown by Runs 11 and 12. Conversion drop was important when the temperature was lowered from 410°C to 356°C. Actually, the conversions and product distribution calculated at 356°C for Run 12 were only rough estimates due to the high dilution of the reaction products in the unconverted feed. The selectivity for C_5^+ fraction increased slightly but this did not compensate for the loss of conversion in regard to the production of liquid hydrocarbons.

Conversions increased with residence time (Runs 12 to 14). Selectivities changed slightly in the C_5^+ fraction where production distributions seemed to move towards a higher content of C_{10} and C_{11}^+ (Runs 13 and 14).

A last series of tests was conducted in order to optimize the catalyst performance for gasoline production. The results are presented in the Tables 9 to 14.

Effect of the method of preparation on the Methanol Synthesis (MSC) Component (Table 9).

The activity of two catalysts with the same composition:

70%wt Zn/Cr 25/75 + 30%wt H-ZSM5

are compared. Their MSC component was prepared according to two different methods: the commercial or wet impregnation method (Runs 16 and 17) and the

Run #	11	12	13	14	15
Zn/Cr atomic ratio	25/75	25/75	25/75	25/75	25/75
pretreatment as	Runs 10 + 12 + 15	Run 10	Runs 10 + 12 + 15 + 11	Runs 10 + 12 + 15 + 11 + 13	Runs 10 + 12
H_2/CO	1	1	1	1	1
P (psig)	640	500	500	500	300
T (°C)	409	356	356	356	356
Flow (mmole/gr.cat/min)	2.9	2.9	0.5	0.2	1.4
CO Conversion	11.0-11.3	4.4-3.0	13.0-7.5	20.3-14.3	4.7-3.1
H_2 Conversion	4.7-6.6	~0	9.5-2.4	8.2-3.7	2.5-1.7
Product Distribution (wt%)					
CO_2	66.4	44.7[a]	71.8	70.5	68.9
H_2O	7.7	8.0	3.3	3.6	9.6
HC	25.9	47.3	24.8	25.8	21.5
CH_3OH	0	0	0	0	0
Liquid Collected (g)					
HC[b]	2.5	0.2	0.25	0.21	0.12
H_2O	0.0	0.0	0.0	0.0	0.0
Total Test Time (min)	370	200	170	360	350
Hydrocarbon Distribution (wt%)					
CH_4	4.0	2.5	3.0	3.0	7.2
$C_2^=$	2.2	1.6	0.8	0.3	6.1
C_2	6.4	1.2	2.7	2.9	4.8
$C_3^=$	0	0.3	0	0	1.2
C_3	8.5	1.8	6.0	5.4	4.8
C_4's	4.3	0.6	1.4	1.2	2.2
C_5^+	74.6	92.0	86.1	87.2	73.7
C_5^+ Distribution (wt%)					
C_5	3.6	4.2	0.8	0.7	1.6
C_6	1.6	1.6	0.3	0.2	1.1
Toluene	2.3	3.2	1.5	1.2	2.6
C_8 Aromatics	20.5	25.9	11.9	8.9	16.5
C_9 Aromatics	41.8	48.5	33.9	29.1	44.9
C_{10} Aromatics	12.5	14.6	23.6	31.9	14.7
C_{11}^+	~15.0	~4.2	~25.0	~25.0	10.9

a - Chromatographic peaks were very small, resulting in important errors in the calculation of this product distribution.

b - Due to an important vapour entrainment in the trap, maintained at 0°C, this fraction is smaller than the total C_5^+ weight fraction.

Note: - First and second reported values are the conversion observed respectively at the beginning of the run and at the end of the run.

Table 8: Catalyst Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of Operating Conditions.

Run #	16	17	18
Catalyst Composition	70% Zn/Cr 25/75 Impregn. Method 30% H-ZSM5	70% Harshaw Cat. 30% H-ZSM5	70% Zn/Cr 25/75 Oct. 87 Batch 30% H-ZSM5
Pretreatment	Calcined 550°C He/400°C	He/400°C	Calcined 350°C He/400°C
H_2/CO ratio	1	1	1
P (sig)	640	640	640
T (°C)	405	405	408
Feed Flowrate			
(mlSTP/min)	1059	1059	1059
(mmole/gr.cat/min)	3.0	3.0	2.9
CO Conversion (%)*	14.9-5.9	18.0-15.4	7.3-10.4
H_2 Conversion (%)	13.3-4.1	13.4-12.5	2.1-5.0
Product Distribution (wt%)			
CO_2	66.4	67.1	69.7
H_2O	6.9	3.1	4.4
HC	26.7	29.8	25.9
CH_3OH	0	0	0
Liquid Collected (g)			
H_2O (g)	0	0	0
HC (g)	0.13	0	2.80
Test Time (min)	310	440	390
Hydrocarbon Distribution (wt%)			
CH_4	23.9	13.1	3.1
$C_2^=$	2.2	2.2	3.1
C_2	8.0	10.3	9.1
$C_3^=$	1.3	1.2	0.9
C_3	15.5	7.8	5.2
C_4's	12.4	19.6	2.1
C_5^+	36.7	45.8	76.4
C_5^+ Distribution (wt%)			
C_5	17.3	50.8	2.0
C_6	7.2	36.2	1.5
Toluene	4.2	3.5	2.4
C_8 Aromatics	28.9	2.4	26.3
C_9 Aromatics	27.2	1.3	44.8
C_{10} Aromatics	5.6	1.6	14.7
C_{11}^+	4.3	1.6	8.3

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 9: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Method of Preparation of the Methanol Synthesis Component.

co-precipitation method (Run 18). Those methods were described in the previous chapter (Section I-C).

The catalyst prepared following a technique similar to the one used for the preparation of the commercial catalyst, showed a rapid activity decrease as measured by the CO and H2 conversions, to reach a level similar to the activity displayed by the co-precipitated catalyst. However the gasoline productivity of the "wet method" catalyst is much lower than the "co-precipitation" catalyst. This resulted in a poor selectivity for C_5^+ as indicated by the hydrocarbon distribution. Moreover, the fraction of methane produced on the "wet method" sample was quite important.

For comparison, results obtained with a commercial HARSHAW catalyst as the MSC component are also given in Table 9 (Run 17). This catalyst is likely prepared according to the wet impregnation method, and has a high Zn/Cr ratio, close to 75/25. Due to its high content of ZnO, the CO and H_2 conversions were important as well as the hydrogenation activity resulting in a low quantity of liquid hydrocarbons (high selectivity for the C_2-C_6 paraffins).

As a consequence, the co-precipitation method gave the most performing catalyst in term of aromatic production, probably due to a better intermixing of the ZnO and Cr_2O_3 oxides. However, the poor performance of the sample prepared according to the wet impregnation method could be the result of an excess of Chromium oxide and/or of the high pretreatment temperature required for the formation of Cr_2O_3 from CrO_3. Indeed, this preparation technique involves an acidic attack of the ZnO surface by the Chromic acid. Consequently, a smaller bulk proportion of the Chromium component may be required in order to achieve a 25/75 Zn/Cr atomic ratio in the superficial layers of the catalyst particules. So, it appeared that it may be interesting to do further research with the commercial method of preparation using higher bulk atomic Zn/Cr ratio. This method might be much less time-consuming and much cheaper than the co-precipitation method.

MSC preparation reproducibility (Table 10)

The MSC component of the two catalysts studied (Runs 10 and 18 on Table 10) belongs to two different batches: respectively a 40g batch (July 87) and a 750g batch (October 1987). The last one was prepared for the catalytic tests in the pilot unit.

The sample from the October 87 batch MSC component seems to have lower activity, as shown by the syngas conversions. Althought this last sample has a slightly higher C_5^+ selectivity, the liquid hydrocarbon yield of the July 87 batch was higher. The C_5^+ hydrocarbon distributions were very similar.

Effect of the Binder Addition (Table 11)

The pellets prepared by dry compression of the ZSM5 and MSC components powder mixture were not hard enough to be utilized in the pilot unit fixed bed. Higher compaction pressure should be used but the appropriate equipment to achieve such pressures was not available. As a consequence, the addition of an Al_2O_3 binder was considered. It has the advantages of a relatively easy preparation of a well shaped 1/8" cylindrical pellet by extrusion. However, the density of the catalyst prepared by extrusion is much lower, as compared to

Run #	10	18
Catalyst Composition	75% Zn/Cr 25/75 July 87 Batch 30% H-ZSM5	70% Zn/Cr 25/75 Oct. 87 Batch 30% H-ZSM5
Pretreatment	Calcined 350°C He/400°C	Calcined 350°C He/400°C
H_2/CO ratio	1	1
P (sig)	640	640
T (°C)	410	408
Feed Flowrate		
(mlSTP/min)	1058	1059
(mmole/gr.cat/min)	2.7	2.9
CO Conversion (%)*	22.9-14.7	7.3-10.4
H_2 Conversion (%)	13.4-6.9	2.1-5.0
Product Distribution (wt%)		
CO_2	70.2	69.7
H_2O	5.3	4.4
HC	24.5	25.9
CH_3OH	0	0
Liquid Collected (g)		
H_2O (g)	0	0
HC (g)	2.93	2.80
Test Time (min)	360	390
Hydrocarbon Distribution (wt%)		
CH_4	6.3	3.1
$C_2^=$	1.2	3.1
C_2	4.6	9.1
$C_3^=$	0	0.9
C_3	10.4	5.2
C_4's	3.6	2.1
C_5^+	73.9	76.4
C_5^+ Distribution (wt%)		
C_5	2.4	2.0
C_6	0.6	1.5
Toluene	3.2	2.4
C_8 Aromatics	26.2	26.3
C_9 Aromatics	40.9	44.8
C_{10} Aromatics	7.7	14.7
C_{11}^+	15.9	8.3

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 10: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Reproducibility of the Preparation (Co-Precipitation Method) of the Methanol Synthesis Component.

Run #	20	21	22
Catalyst Composition	49% Zn/Cr 25/75 Oct. 87 Batch 21% H-ZSM5 30% Binder	63% Zn/Cr 25/75 Oct. 87 Batch 27% H-ZSM5 10% Binder	70% Zn/Cr 25/75 Oct. 87 Batch 30% H-ZSM5
Pretreatment	Calcined 350°C He/400°C	Calcined 350°C He/400°C	Calcined 350°C He/400°C
H_2/CO ratio	1	1	1
P (sig)	640	500	640
T (°C)	406	410	408
Feed Flowrate			
(mlSTP/min)	628	771	1059
(mmole/gr.cat/min)	2.6	2.3	2.9
CO Conversion (%)*	15.5-6.0	7.2-2.6	7.3-10.4
H_2 Conversion (%)	13.6-7.0	3.8-0.0	2.1-5.0
Product Distribution (wt%)			
CO_2	63.4	69.0	69.7
H_2O	7.4	4.9	4.4
HC	29.2	26.2	25.9
CH_3OH	0	0	0
Liquid Collected (g)			
H_2O (g)	0	0	0
HC (g)	1.05	1.15	2.80
Test Time (min)	420	380	390
Hydrocarbon Distribution (wt%)			
CH_4	14.2	5.3	3.1
$C_2^=$	3.0	2.0	3.1
C_2	3.8	5.1	9.1
$C_3^=$	0.9	0.7	0.9
C_3	5.4	6.3	5.2
C_4's	2.5	2.9	2.1
C_5^+	70.2	77.7	76.4
C_5^+ Distribution (wt%)			
C_5	2.2	1.7	2.0
C_6	1.7	2.7	1.5
Toluene	2.0	3.6	2.4
C_8 Aromatics	27.0	28.2	26.3
C_9 Aromatics	39.0	38.3	44.8
C_{10} Aromatics	13.1	10.6	14.7
C_{11}^+	6.3	13.5	8.3

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 11: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Binder Addition.

the density of the pellets obtained by dry compaction. Besides, the MSC component was partially attacked by the residual acidity of the pseudoboehmite binder. In order to limit this effect, which could be detrimental to the catalyst activity, the pellets were quickly dried at 110°C, after being formed by extrusion.

Three levels of binder concentration were tested: 0% (Run 18), 10%, (Run 21) and 30% (Run 20). The effect of dilution of the active component was compensated by adjusting the inlet reactant flow. The addition of the binder was accompanied by a decrease of the activity of the catalyst as well as an important deactivation during the catalytic run. When the binder proportion was 30%, CH4 production seemed to be enhanced and C_5^+ selectivity was decreased. The C_5^+ hydrocarbon distribution was barely affected by the binder presence. Liquid hydrocarbon yields were reduced by the binder addition although the quantities of those fractions were not readily comparable for Run 21 (10% binder) and Run 18 (no binder). Actually, in accordance with the lower operating pressure (500 psig against 640 psig) and a lower inlet flow rate, it is expected that the liquid fraction collected in Run 21 should be higher, if obtained under conditions identical to those of Run 18.

Because the addition of only 10% binder resulted in pellets being resistant enough to attrition, this formulation was selected for the preparation of the catalyst to be used in the pilot unit.

Effect of the catalyst pretreatment (Tables 12 and 13)

Essentially, two pretreatment parameters were considered:

a) the calcination temperature of the dry mixture (Tables 12 and 13),

b) the prereduction of the catalyst (Table 13).

In Table 12, the activities of a non-precalcined sample (Run 19) and of a sample precalcined at the standard temperature, 350°C, (Run 20) are compared. The main effect of the absence of calcination is a very quick activity decay, resulting in an almost total loss of activity of the catalyst.

In Table 13, it is observed that a high precalcination temperature, 450°C (Run 22) against 350°C (Run 21), is detrimental to the catalyst activity. On the contrary, an additional prereduction of the catalyst at 300-310°C with diluted H_2 in He (Run 23) results in several improvements:

- a higher CO and H_2 conversion
- more stable activity as indicated by the conversions at the beginning and at the end of the run.

Although the C_5^+ selectivity was significantly lowered with the prereduced sample when compared with the calcined-only sample, the better activity and resistance to deactivation lead to an overall higher liquid yield.

The observed effects are believed to be the result of a better control of the catalyst reduction step. Indeed, BET surface area measurement have shown that the area of exposed surface of the MSC component is lowered by a factor of 3 when pretreated at 400°C under Helium then exposed to the reducing atmosphere

Run #	19	20
Catalyst Composition	49% Zn/Cr 25/75 Oct. 87 Batch 21% H-ZSM5 31% Binder	49% Zn/Cr 25/75 Oct. 87 Batch 21% H-ZSM5 30% Binder
Pretreatment	Dried 110°C He/400°C	Calcined 350°C He/400°C
H_2/CO ratio	1	1
P (sig)	640	640
T (°C)	408	406
Feed Flowrate		
(mlSTP/min)	628	628
(mmole/gr.cat/min)	2.6	2.6
CO Conversion (%)*	12.0-0.5	15.5-6.0
H_2 Conversion (%)	11.0-0.0	13.6-7.0
Product Distribution (wt%)		
CO_2	47.5[a]	63.4
H_2O	2.3	7.4
HC	50.2	29.2
CH_3OH	0	0
Liquid Collected (g)		
H_2O (g)	0	0
HC (g)	0	1.05
Test Time (min)	180	420
Hydrocarbon Distribution (wt%)		
CH_4	23.5	14.2
$C_2^=$	4.5	3.0
C_2	16.7	3.8
$C_3^=$	1.4	0.9
C_3	7.7	5.4
C_4's	7.4	2.5
C_5^+	38.8	70.2
C_5^+ Distribution (wt%)		
C_5	4.5	2.2
C_6	2.1	1.7
Toluene	3.9	2.0
C_8 Aromatics	31.2	27.0
C_9 Aromatics	40.5	39.0
C_{10} Aromatics	15.0	13.1
C_{11}^+	2.7	6.3

a - Chromatographic peaks were very small, resulting in important errors in the calculation of this product distribution.

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 12: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Catalyst Pretreatment.

Run #	22	21	23
Catalyst Composition	63% Zn/Cr 25/75 Oct. 87 Batch 27% H-ZSM5 10% Binder	63% Zn/Cr 25/75 Oct 87 Batch 27% H-ZSM5 10% Binder	63% Zn/Cr 25/75 Oct. 87 Batch 27% H-ZSM5 10% Binder
Pretreatment	Calcined 450°C He/400°C	Calcined 350°C He/400°C	Calcined 350°C 7.8% H_2 in He/310°C
H_2/CO ratio	1	1	1
P (psig)	510	510	510
T (°C)	410	410	405
Feed Flowrate			
(mlSTP/min)	777	771	782
(mmole/gr.cat/min)	2.3	2.3	2.3
CO Conversion (%)*	2.5-0.9	7.2-2.6	25.1-20.6
H_2 Conversion (%)	1.4-0.0	3.8-0.0	10.6-11.6
Product Distribution (wt%)			
CO_2	53.9	69.0	72.7
H_2O	4.6	4.9	2.4
HC	41.4	26.2	24.9
CH_3OH	0	0	0
Liquid Collected (g)			
H_2O (g)	0	0	0
HC (g)	0.25	1.15	3.20
Test Time (min)	430	380	320
Hydrocarbon Distribution (wt%)			
CH_4	10.6	5.3	4.7
$C_2^=$	2.6	2.0	1.0
C_2	8.9	5.1	12.1
$C_3^=$	1.0	0.7	0.5
C_3	10.2	6.3	15.2
C_4's	5.2	2.9	5.8
C_5^+	61.5	77.7	60.7
C_5^+ Distribution (wt%)			
C_5	4.3	1.7	4.0
C_6	1.8	2.7	0.7
Toluene	5.0	3.6	2.7
C_8 Aromatics	34.0	28.2	25.5
C_9 Aromatics	35.8	38.3	39.8
C_{10} Aromatics	8.0	10.6	14.1
C_{11}^+	10.2	13.5	10.1

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 13: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Catalyst Pretreatment.

of the syngas feed, relatively to the sample submitted to the reduction pretreatment. In accordance with those results, it was decided that, for the following phases of the program, the standard catalyst pre-treatment would be:

1. Heating the sample from room temperature to 350°C, temperature maintained for 2 hours, in an oven under static air;
2. Then heating the sample from room temperature to 300°C, in the reactor, under a stream of diluted H_2 (8% or less H_2 in He).

The temperature of 300°C for the reduction pretreatment was selected in accordance with the observations made during the BET surface area experiments described in the previous chapter: complete prereduction of the $ZnO\text{-}Cr_2O_3$ samples was achieved in all cases at temperatures lower than 300°C. This was confirmed during the pretreatment in the Berty reactor as no more water, product of the reduction of the oxidized MSC component, was observed at higher temperatures.

Effect of the Zn/Cr atomic ratio in the MSC component (Table 14)

The influence of this parameter was again studied in order to see if the new pretreatment procedure, including the prereducing step, could change the previous observations. The catalytic performances of 2 samples differing by the Zn/Cr ratio of their MSC component (25/75 (Run 23) and 50/50 (Run 24) are compared in Table 14. Those results show that, actually, the prereduction treatment does not modify the previously observed effects of Zn/Cr atomic ratio. A higher zinc proportion results in a higher activity but, also in a lower C_5^+ selectivity. The overall result is a reduction of the liquid yield.

The C_5^+ product distribution also shows a lower amount of aromatics indicating

Run #	23	24
Catalyst Composition	63% Zn/Cr 25/75 Oct. 87 Batch 27% H-ZSM5 10% Binder	63% Zn/Cr 50/50 27% H-ZSM5 10% Binder
Pretreatment	Calcined 350°C 7.8% H_2 in He/310°C	Calcined 350°C 7.8% H_2 in He/310°C
H_2/CO ratio	1	1
P (psig)	510	510
T (°C)	405	405
Feed Flowrate		
(mlSTP/min)	782	640
(mmole/gr.cat/min)	2.6	2.2
CO Conversion (%)*	25.1-20.6	40.1-34.3
H_2 Conversion (%)	10.6-11.6	29.5-26.1
Product Distribution (wt%)		
CO_2	72.7	69.1
H_2O	2.4	3.2
HC	24.9	27.6
CH_3OH	0	0
Liquid collected (g)		
H_2O (g)	0	0
HC (g)	3.2	2.55
Test Time (min)	320	320
Hydrocarbon Distribution (wt%)		
CH_4	4.7	5.5
$C_2^=$	1.0	0.9
C_2	12.1	4.0
$C_3^=$	0.5	0.7
C_3	15.2	27.1
C_4's	5.8	18.1
C_5^+	60.7	43.7
C_5^+ Distribution (wt%)		
C_5	4.0	20.3
C_6	0.7	5.9
Toluene	2.7	2.3
C_8 Aromatics	25.5	21.2
C_9 Aromatics	39.8	26.0
C_{10} Aromatics	14.1	10.6
C_{11}^+	10.1	7.1

Note: * First and second reported values are the conversions observed respectively at the beginning of the run and at the end of the run.

Table 14: Catalytic Test Results for Syngas Conversion to Hydrocarbons in the Berty Reactor. Effect of the Zn/Cr Atomic Ratio.

the higher hydrogenation activity of the catalyst with the high zinc content.

5. Kinetic Study.

43 kinetic runs were performed as part of this program. The catalyst formulation was as follows:

- 63% $ZnO-Cr_2O_3$ (Zn/Cr = 1/3 at.)
- 27% H-ZSM5
- 10% Versal 950 (Al_2O_3 binder)

Three series of runs at three different temperatures, 355°C, 375°C, and 405°C, were conducted. For each series of runs, a new batch of catalyst (around 15 g) was used. The catalyst sample was subjected to a calcination at 350°C for 2 hours, followed by an in-situ reduction at 300°C in a stream of 7.8% H_2 diluted in He. During the reduction period, the reactor temperature was risen slowly from the room temperature to 300°C and maintained at this level for 16 hours. Between each kinetic run, the catalyst was kept in the reactor under Helium flow (290-300°C). The operating conditions for each run were a combination of the following values:

- for the pressure :300, 400, 500, 600 psig
- for the WHSV :890, 1930, 2600 ml STP/g cat./hr
- for the H2/CO :1, 2.

It has to be pointed out that a run was repeated under identical operating conditions to assess the catalyst decay. Run conditions, conversions, product distributions and mass balances are reported in Tables 15a-b, 16a-b, 17a-b, 18a-b, 19a-b and 20a-b.

Mass balances were closed within 6% and, for the majority of the runs within 2.5%. CO conversions varied between 6 and 35%.

It was observed that, under the operating conditions used in the kinetic study, the water gas shift reaction:

$$CO + H_2O \;=\; CO_2 + H_2$$

was at equilibrium, and the methanol formed was totally converted to hydrocarbons. As a consequence, the kinetics of the limiting reaction step, the methanol synthesis on the $ZnO\text{-}Cr_2O_3$ component, is the one that controls the overall rate of reaction. Further in the kinetic modelling, the hydrogenation on the $ZnO\text{-}Cr_2O_3$ component of the olefinic intermediates, formed in the transformation of methanol to liquid hydrocarbons, is neglected. The kinetic equation, similar to the one proposed by Natta (1955), to describe the rate of CO conversion to methanol on a $ZnO\text{-}Cr_2O_3$ catalyst, was chosen to fit the data of the 43 kinetic runs. This form of the equation corresponds to the case where the limiting step is the surface reaction between molecular adsorbed H_2 and CO reactants. A Marquardt algorithm was used to calculate the best estimates for the 9 parameters to be determined. A copy of the computer program is enclosed in Appendix E.

RUN #	880506A*	880509A	880509B	880510A*	880510B	880511A	880511B
OPERATING CONDITIONS							
Temperature (°C)	356.00	355.00	354.00	356.00	356.50	354.50	355.00
Pressure (atm.)	42.20	42.50	28.20	42.50	28.20	34.70	34.70
H_2/CO molar	1.14	1.13	1.12	1.13	1.11	1.11	1.10
Feed Flowrate (mole/sec)	159.80	356.10	356.10	159.10	158.40	349.90	157.00
WHSV (ml STP/g_{cat}/hr)	891.00	1985.00	1985.00	887.00	883.00	1950.00	875.00
Test Duration (min)	237.00	194.00	201.00	160.00	235.00	201.00	197.00
Cum. Time on stream (min)	150.00	340.00	580.00	730.00	960.00	1150.00	1330.00
CONVERSIONS							
H_2	13.3	6.7	4.9	11.5	8.8	5.6	9.2
CO	25.3	13.1	9.0	19.1	15.6	9.8	16.4
PRODUCT MASS DISTRIBUTION							
CO_2	76.6	74.1	71.8	72.6	71.4	71.6	68.9
H_2O	2.0	2.5	3.7	2.3	2.5	3.6	2.9
Hydrocarbons	21.4	23.4	24.5	25.1	26.1	24.8	28.2
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)							
C	-0.7	-0.5	0.2	1.8	0.8	0.0	1.7
H	-3.5	-1.1	-0.3	-1.8	-0.6	-0.5	0.0
O	1.5	-0.1	0.4	1.6	0.3	0.1	0.1
TOTAL	0.2	-0.3	0.3	1.3	0.4	0.0	0.8

* : Run conducted at standard operating conditions to assess activity decay.

Table 15a: Results of the syngas conversion kinetic runs in the Berty Reactor at 355°C. Catalyst: 63% ZnO-Cr_2O_3 (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880512A*	880513A	880513B	880516A	880516B	880517A*
OPERATING CONDITIONS						
Temperature (°C)	356.00	355.50	354.00	354.00	356.00	356.50
Pressure (atm.)	42.20	42.70	35.40	28.20	41.80	41.80
H_2/CO molar	1.13	2.42	2.14	2.31	2.21	1.12
Feed Flowrate (mole/sec)	155.00	157.70	159.80	159.10	354.00	156.00
WHSV (ml STP/g_{cat}/hr)	864.00	879.00	891.00	887.00	1973.00	869.00
Test Duration (min)	254.00	152.00	165.00	160.00	191.00	179.00
Cum. Time on stream (min)	1570.00	1770.00	1930.00	2100.00	2280.00	2440.00
CONVERSIONS						
H_2	10.3	11.0	7.6	6.0	4.7	11.2
CO	15.9	19.7	21.5	14.7	14.2	17.2
PRODUCT MASS DISTRIBUTION						
CO_2	72.8	67.4	69.4	65.0	66.7	73.0
H_2O	2.0	5.0	5.1	6.3	6.8	4.0
Hydrocarbons	25.2	27.6	25.5	28.7	26.5	23.0
Methanol	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)						
C	3.1	10.0	1.9	5.2	2.0	0.8
H	-1.2	-2.7	-0.5	0.0	0.0	-1.8
O	2.8	8.7	2.2	4.0	2.0	2.1
TOTAL	2.6	6.0	1.8	4.5	2.0	1.2

* : Run conducted at standard operating conditions to assess activity decay.

Table 15b: Results of the syngas conversion kinetic runs in the Berty Reactor at 355°C. Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880506A*	880509A	880509B	880510A*	880510B	880511A	880511B
Methane	3.2	4.0	4.9	4.2	4.7	5.1	4.7
Ethylene	0.4	2.2	3.1	1.6	2.1	3.6	1.8
Ethane	3.0	8.0	10.9	9.0	11.1	11.4	9.8
Propylene	0.2	0.7	1.2	0.5	0.8	1.5	0.6
Propane	13.8	10.3	8.7	10.3	9.4	7.7	7.7
i-Butane	2.0	2.6	3.1	2.5	2.9	3.2	2.3
n-Butane	2.3	2.6	2.1	2.4	2.2	1.9	1.8
Butenes	0.1	0.4	0.6	0.3	0.4	0.8	0.3
C_5^+ Hydrocarbons							
Paraffins + Cycloparaffins	3.7	7.4	9.6	6.1	7.2	9.7	6.1
Olefins + Cycloolefins	0.0	0.1	0.3	0.1	0.6	0.2	0.1
Aromatics	56.3	55.4	50.2	55.9	50.8	50.4	56.7
C_{11}^+	15.0	6.3	5.3	7.1	7.8	4.5	8.1
C_5^+ Hydrocarbons Product Distribution							
C_5 - C_8 Saturates	5.0	10.7	14.6	8.7	10.8	15.0	8.5
C_5 - C_8 Unsaturates	0.0	0.1	0.4	0.2	0.8	0.3	0.2
C_9^+ P+O+N	0.0	0.0	0.0	0.1	0.1	0.0	0.1
Benzene	0.4	0.4	0.4	0.2	0.3	0.4	0.2
Toluene	2.8	2.2	2.1	1.5	1.5	1.7	1.1
C_8 Aromatics	18.7	18.1	18.1	12.9	13.2	14.7	10.8
C_9 Aromatics	35.3	37.7	36.8	34.5	34.1	36.0	33.6
C_{10} Aromatics	17.8	21.7	19.4	31.6	27.5	24.9	34.1
C_{11} Aromatics	8.2	4.9	4.6	5.9	5.9	4.7	6.9
C_{12} Aromatics	7.7	2.6	2.0	2.2	2.3	1.1	2.6
C_{13} Aromatics	3.3	1.2	1.1	1.3	2.2	1.0	1.4
C_{14} Aromatics	0.7	0.4	0.3	0.6	0.7	0.0	0.3
C_{15} Aromatics	0.1	0.0	0.2	0.3	0.8	0.2	0.2

* : Run conducted at standard operating conditions to assess activity decay.

Table 16a: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 355°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880512A*	880513A	880513B	880516A	880516B	880517A*
Methane	5.0	5.1	5.1	4.6	4.6	5.1
Ethylene	2.2	1.7	2.0	2.3	2.9	2.4
Ethane	10.6	11.3	11.5	13.4	11.1	10.9
Propylene	0.8	0.6	0.7	1.0	1.1	0.7
Propane	9.3	14.3	14.0	13.3	11.8	10.9
i-Butane	2.7	4.9	4.7	5.1	4.4	2.9
n-Butane	2.2	3.7	3.4	3.2	3.3	2.5
Butenes	0.4	0.3	0.3	0.4	0.5	0.5
C_5^+ Hydrocarbons						
Paraffins + Cycloparaffins	7.2	11.0	11.1	12.3	12.1	7.6
Olefins + Cycloolefins	0.3	0.2	0.1	0.1	0.4	0.1
Aromatics	53.1	42.4	43.6	41.5	43.1	50.7
C_{11}^+	6.2	4.5	3.5	2.8	4.7	5.8
C_5^+ Hydrocarbons Product Distribution						
C_5 - C_8 Saturates	10.7	18.8	19.0	21.7	19.7	11.8
C_5 - C_8 Unsaturates	0.4	0.3	0.1	0.2	0.6	0.1
C_9^+ P+O+N	0.0	0.2	0.0	0.0	0.3	0.0
Benzene	0.2	0.2	0.3	0.3	0.3	0.3
Toluene	1.4	1.5	1.7	1.8	1.6	1.5
C_8 Aromatics	11.5	11.9	13.9	15.5	13.6	13.3
C_9 Aromatics	33.3	30.5	32.9	33.5	32.0	29.2
C_{10} Aromatics	33.2	28.8	26.2	22.1	24.1	34.8
C_{11} Aromatics	6.2	4.9	4.4	3.5	4.7	6.2
C_{12} Aromatics	1.8	1.6	1.1	0.8	1.5	2.0
C_{13} Aromatics	1.1	0.8	0.4	0.6	1.0	0.8
C_{14} Aromatics	0.1	0.3	0.0	0.0	0.2	0.0
C_{15} Aromatics	0.1	0.2	0.1	0.0	0.4	0.0

* : Run conducted at standard operating conditions to assess activity decay.

Table 16b: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 355°C.
Catalyst: 63% $ZnO\text{-}Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880519A*	880520A	880520B	880524A*	880524B	880525A	880525B	880526A*
OPERATING CONDITIONS								
Temperature (°C)	375.00	376.50	375.00	375.50	374.00	374.50	375.00	374.00
Pressure (atm.)	42.50	42.10	35.00	42.30	35.40	28.40	27.90	41.60
H_2/CO molar	1.15	1.14	1.10	1.17	1.03	1.03	1.10	1.12
Feed Flowrate (mole/sec)	154.30	347.10	155.60	155.00	343.70	354.70	159.10	156.70
WHSV (ml STP/g_{cat}/hr)	860.00	1935.00	868.00	864.00	1916.00	1977.00	887.00	873.00
Test Duration (min)	227.00	179.00	142.00	292.00	130.00	163.00	167.00	213.00
Cum. Time on stream (min)	150.00	330.00	500.00	650.00	940.00	1120.00	1270.00	1450.00
CONVERSIONS								
H_2	18.0	11.7	14.9	18.2	6.6	9.9	14.6	16.1
CO	34.2	17.6	25.5	25.1	15.9	12.7	19.0	25.5
PRODUCT MASS DISTRIBUTION								
CO_2	73.7	72.3	70.2	73.3	72.2	70.6	71.5	71.5
H_2O	2.2	2.3	3.3	2.5	2.8	3.7	2.6	2.3
Hydrocarbons	24.1	25.4	26.5	24.2	25.0	25.7	25.9	26.2
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)								
C	3.8	1.9	1.5	3.3	-0.5	0.4	2.4	1.2
H	-2.4	-2.7	-0.6	-5.4	1.4	-1.9	-3.0	-2.4
O	4.3	1.5	0.4	3.8	-0.4	0.4	1.9	0.2
TOTAL	3.2	1.2	0.8	2.2	-0.3	0.2	1.5	0.4

* : Run conducted at standard operating conditions to assess activity decay.

Table 17a: Results of the syngas conversion kinetic runs in the Berty Reactor at 375°C. Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880601A*	880621A*	880622A	880622B	880623A	880623B	880627A*
OPERATING CONDITIONS							
Temperature (°C)	374.00	374.00	375.00	375.50	374.00	376.00	375.50
Pressure (atm.)	41.80	42.20	41.80	35.00	28.10	41.50	41.90
H_2/CO molar	1.19	1.16	2.34	2.26	2.32	2.25	1.10
Feed Flowrate (mole/sec)	156.30	157.00	158.40	157.00	158.70	340.90	153.60
WHSV (ml STP/g_{cat}/hr)	871.00	889.00	896.00	875.00	898.00	1929.00	869.00
Test Duration (min)	185.00	250.00	157.00	147.00	210.00	153.00	229.00
Cum. Time on stream (min)	1620.00	1890.00	2050.00	2210.00	2400.00	2560.00	2770.00
CONVERSIONS							
H_2	17.2	14.8	9.8	7.0	10.3	5.4	13.7
CO	23.2	22.3	27.8	26.8	22.9	20.7	22.0
PRODUCT MASS DISTRIBUTION							
CO_2	71.8	68.7	67.8	66.8	67.2	66.5	70.4
H_2O	2.3	2.4	4.6	4.8	6.2	6.0	3.3
Hydrocarbons	25.9	28.9	27.6	28.4	26.6	27.5	26.3
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)							
C	4.0	7.9	7.2	6.6	2.5	1.7	3.9
H	-4.1	0.0	0.0	2.8	-2.7	1.1	0.0
O	3.2	4.6	5.6	4.4	2.5	1.0	3.2
TOTAL	2.4	6.0	6.3	4.0	1.4	1.2	3.5

* : Run conducted at standard operating conditions to assess activity decay.

Table 17b: Results of the syngas conversion kinetic runs in the Berty Reactor at 375°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880519A*	880520A	880520B	880524A*	880524B	880525A	880525B	880526A*
Methane	3.4	4.5	4.9	5.2	5.4	6.2	5.8	5.5
Ethylene	0.3	1.5	1.0	1.1	2.3	2.7	1.6	1.4
Ethane	3.8	8.9	9.8	9.7	12.6	15.0	14.9	11.9
Propylene	0.1	0.6	0.4	0.4	1.0	1.5	0.8	0.5
Propane	15.2	11.7	12.1	11.5	9.8	9.8	10.9	10.7
i-Butane	2.3	3.0	2.9	2.9	3.7	5.5	4.4	3.1
n-Butane	2.3	2.7	2.5	2.5	2.3	2.2	2.3	2.3
Butenes	0.1	0.3	0.2	0.2	0.5	0.7	0.4	0.3
C_5^+ Hydrocarbons								
Paraffins + Cycloparaffins	3.3	7.0	5.8	6.0	9.1	12.1	8.4	6.8
Olefins + Cycloolefins	0.1	0.1	0.1	0.1	0.2	0.3	0.1	0.1
Aromatics	54.1	52.5	53.3	54.1	48.9	41.3	46.6	52.0
C_{11}^+	15.0	7.2	7.0	6.3	4.2	2.7	3.7	5.4
C_5^+ Hydrocarbons Product Distribution								
C_5 - C_8 Saturates	4.5	10.5	8.7	9.1	14.7	21.5	14.3	10.6
C_5 - C_8 Unsaturates	0.1	0.1	0.2	0.1	0.2	0.5	0.2	0.1
C_9^+ P+O+N	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.4	0.4	0.3	0.2	0.3	0.4	0.3	0.2
Toluene	2.9	2.2	1.8	1.5	1.7	1.7	1.5	1.3
C_8 Aromatics	18.6	18.9	15.2	13.5	16.2	16.1	14.0	12.0
C_9 Aromatics	36.8	36.7	37.1	34.9	37.0	35.2	36.4	33.9
C_{10} Aromatics	16.0	20.5	26.1	31.1	23.1	19.8	27.1	33.5
C_{11} Aromatics	8.6	5.0	5.6	5.7	4.2	3.4	4.3	5.6
C_{12} Aromatics	8.2	2.9	2.8	2.1	1.6	0.6	1.3	1.5
C_{13} Aromatics	3.3	1.7	1.5	1.2	0.9	0.6	0.5	1.0
C_{14} Aromatics	0.5	0.9	0.5	0.5	0.0	0.0	0.0	0.2
C_{15} Aromatics	0.1	0.2	0.2	0.1	0.1	0.2	0.1	0.1

* : Run conducted at standard operating conditions to assess activity decay.

Table 18a: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs
in the Berty Reactor at 375°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880601A*	880621A*	880622A	880622B	880623A	880623B	880627A*
Methane	5.5	4.6	5.3	5.2	5.4	4.4	5.2
Ethylene	1.3	1.0	1.3	1.4	1.6	2.2	1.5
Ethane	11.5	9.6	15.6	14.1	16.7	13.8	13.0
Propylene	0.5	0.4	0.6	0.6	0.9	1.0	0.7
Propane	11.0	8.7	14.4	14.6	14.1	12.4	11.2
i-Butane	3.2	2.7	5.4	5.4	6.6	5.1	3.9
n-Butane	2.4	1.9	3.4	3.2	3.1	3.1	2.5
Butenes	0.3	0.2	0.3	0.3	0.4	0.5	0.3
C_5^+ Hydrocarbons							
Paraffins + Cycloparaffins	6.9	5.9	11.2	10.8	12.8	12.6	8.6
Olefins + Cycloolefins	0.1	0.2	0.1	0.1	0.2	0.2	0.1
Aromatics	50.0	55.0	40.1	40.2	34.3	39.9	47.0
C_{11}^+	7.3	9.8	4.4	4.1	3.9	4.8	6.0
C_5^+ Hydrocarbons Product Distribution							
C_5 - C_8 Saturates	10.7	8.3	20.1	19.5	25.0	21.9	13.9
C_5 - C_8 Unsaturates	0.1	0.2	0.2	0.2	0.4	0.3	0.2
C_9^+ P+O+N	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Benzene	0.2	0.2	0.2	0.3	0.3	0.3	0.2
Toluene	1.3	1.0	1.4	1.5	1.4	1.5	1.2
C_8 Aromatics	12.0	10.1	12.5	14.2	14.5	14.0	11.6
C_9 Aromatics	32.4	31.1	30.0	31.4	30.7	31.2	31.9
C_{10} Aromatics	31.9	35.2	27.9	25.6	20.1	22.4	31.2
C_{11} Aromatics	6.4	7.7	4.4	4.2	3.5	3.7	6.1
C_{12} Aromatics	2.3	2.8	1.3	1.4	0.8	1.5	2.0
C_{13} Aromatics	1.6	1.7	1.1	1.1	1.8	3.1	1.0
C_{14} Aromatics	0.7	0.6	0.5	0.4	1.1	0.0	0.5
C_{15} Aromatics	0.4	1.0	0.4	0.2	0.4	0.1	0.2

* : Run conducted at standard operating conditions to assess activity decay.

Table 18b: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs
in the Berty Reactor at 375°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880126A*	880127A	880129A	880201A*	880202A	880202B	880203A*	880203B*
OPERATING CONDITIONS								
Temperature (°C)	400.00	400.00	399.50	399.50	400.50	401.50	401.00	400.00
Pressure (atm.)	35.40	35.70	36.10	35.00	21.60	21.40	21.40	35.00
H_2/CO molar	1.01	1.03	1.00	0.99	0.97	0.97	0.97	0.97
Feed Flowrate (Nmole/sec)	440.80	159.80	907.00	456.30	444.20	157.70	907.00	445.60
WHSV (ml STP/g_{cat}/hr)	2558.00	927.00	5264.00	2648.00	2578.00	915.00	5264.00	2586.00
Test Duration (min)	237.00	260.00	258.00	240.00	157.00	180.00	210.00	205.00
Cum. Time on stream (min)	180.00	340.00	700.00	920.00	1100.00	1270.00	1480.00	1660.00
CONVERSIONS								
H_2	12.6	24.3	9.0	13.6	8.1	14.5	4.0	8.4
CO	21.2	34.6	12.8	18.7	11.5	19.5	6.1	14.2
PRODUCT MASS DISTRIBUTION								
CO_2	70.9	72.1	68.7	68.2	68.3	70.8	70.5	71.4
H_2O	3.1	1.9	3.6	5.3	5.3	3.2	2.9	2.7
Hydrocarbons	26.0	26.0	27.7	26.5	26.4	26.0	26.6	25.9
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)								
C	2.7	2.3	0.2	-0.4	0.8	2.5	1.5	3.5
H	0.2	-4.9	-0.9	-1.5	0.9	0.0	1.3	2.3
O	2.0	1.0	-0.6	-0.6	0.8	2.3	1.4	3.1
TOTAL	2.3	0.9	-0.3	-0.6	0.9	2.4	1.4	3.0

* : Run conducted at standard operating conditions to assess activity decay.

Table 19a: Results of the syngas conversion kinetic runs in the Berty Reactor at 400°C. Catalyst: 63%$ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880415A*	880421A	880421B	880422A	880422B	880425A*	880502A*
OPERATING CONDITIONS							
Temperature (°C)	400.50	400.50	400.50	401.00	400.00	400.00	400.00
Pressure (atm.)	35.00	28.40	28.20	35.10	34.70	34.90	35.30
H_2/CO molar	1.15	1.14	1.08	2.30	2.29	1.16	1.12
Feed Flowrate (mole/sec)	456.60	163.90	362.90	360.90	160.50	450.80	442.80
WHSV (ml STP/g_{cat}/hr)	2650.00	951.00	2107.00	2095.00	931.00	2616.00	2570.00
Test Duration (min)	300.00	271.00	172.00	173.00	160.00	234.00	237.00
Cum. Time on stream (min)	1940.00	2220.00	2420.00	2590.00	2760.00	2970.00	3210.00
CONVERSIONS							
H_2	10.9	17.8	11.6	9.1	13.3	10.1	8.5
CO	13.6	20.2	16.1	22.2	34.4	14.8	13.5
PRODUCT MASS DISTRIBUTION							
CO_2	70.8	70.3	71.6	67.3	67.5	69.8	70.8
H_2O	4.1	3.8	3.6	5.9	5.7	4.1	3.0
Hydrocarbons	25.1	25.9	24.8	26.8	26.8	26.1	26.2
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)							
C	3.9	5.9	-0.7	1.7	0.4	1.8	1.3
H	-1.4	-2.9	-2.7	-1.6	-2.2	-1.0	0.0
O	4.2	5.7	-0.3	1.6	0.1	1.6	1.0
TOTAL	3.6	4.5	-0.5	1.1	-0.1	1.5	1.2

* : Run conducted at standard operating conditions to assess activity decay.

Table 19b: Results of the syngas conversion kinetic runs in the Berty Reactor at 400°C. Catalyst: 63%$ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880126A*	880127A	880129A	880201A*	880202A	880202B	880203A	880203B*
Methane	4.4	5.2	5.9	6.3	9.5	8.3	10.4	6.7
Ethylene	0.9	0.6	2.4	1.8	2.6	1.3	3.9	1.4
Ethane	9.7	10.4	15.2	16.5	21.7	21.3	20.0	17.4
Propylene	0.4	0.3	1.4	1.0	1.8	0.9	3.0	1.1
Propane	15.4	15.0	11.1	11.8	11.7	13.3	10.1	11.2
i-Butane	2.9	2.6	4.4	4.5	9.5	6.5	9.6	4.8
n-Butane	2.8	2.5	2.5	2.5	2.3	2.4	2.1	2.4
Butenes	0.2	0.2	0.6	0.5	0.7	0.4	1.1	0.5
C_5^+ Hydrocarbons								
Paraffins + Cycloparaffins	4.6	3.6	10.4	7.7	11.9	7.1	13.8	7.7
Olefins + Cycloolefins	0.1	0.0	0.2	0.2	0.2	0.1	0.8	0.1
Aromatics	49.1	51.7	42.6	44.0	27.1	35.9	24.1	44.2
C_{11}^+	9.5	7.9	3.3	3.2	1.0	2.5	1.1	2.5
C_5^+ Hydrocarbons Product Distribution								
C_5 - C_8 Saturates	7.2	5.7	17.9	14.0	29.6	15.7	34.6	14.1
C_5 - C_8 Unsaturates	0.1	0.1	0.3	0.3	0.6	0.2	2.1	0.2
C_9^+ P+O+N	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0
Benzene	0.5	0.4	0.5	0.4	0.4	0.3	0.6	0.3
Toluene	2.7	2.3	2.3	2.0	1.9	1.5	2.2	1.8
C_8 Aromatics	25.0	19.5	23.0	19.5	18.7	16.4	19.0	18.0
C_9 Aromatics	38.0	41.0	37.3	40.0	34.1	40.3	30.0	40.5
C_{10} Aromatics	11.4	18.5	12.2	18.0	12.1	20.2	8.9	20.4
C_{11} Aromatics	5.8	5.9	3.2	3.7	1.6	3.6	1.7	3.3
C_{12} Aromatics	5.6	4.0	1.7	1.6	0.7	1.3	0.4	1.4
C_{13} Aromatics	3.0	2.0	1.1	0.5	0.3	0.5	0.3	0.0
C_{14} Aromatics	0.5	0.6	0.0	0.0	0.0	0.0	0.0	0.0
C_{15} Aromatics	0.2	0.0	0.0	0.0	0.0	0.0	0.2	0.0

* : Run conducted at standard operating conditions to assess activity decay.

Table 20a: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 400°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

RUN #	880415A*	880421A	880421B	880422A	880422B	880425A*	880502A*
Methane	6.6	7.6	8.0	7.2	7.6	6.6	7.9
Ethylene	1.9	1.2	2.1	1.7	1.0	2.1	2.4
Ethane	16.5	18.6	18.6	20.0	19.3	16.4	17.5
Propylene	1.1	0.8	1.4	1.1	0.6	1.3	1.6
Propane	11.0	12.6	11.2	14.6	16.3	10.4	10.4
i-Butane	4.7	5.6	6.9	7.5	6.2	5.6	7.1
n-Butane	2.4	2.4	2.4	3.2	3.3	2.4	2.3
Butenes	0.6	0.4	0.6	0.5	0.3	0.6	0.7
C_5^+ Hydrocarbons							
Paraffins + Cycloparaffins	9.0	7.2	10.4	13.0	9.2	11.0	13.3
Olefins + Cycloolefins	0.2	0.1	0.3	0.2	0.1	0.3	0.6
Aromatics	42.7	39.0	34.0	29.5	33.8	37.8	33.9
C_{11}^+	3.3	4.5	2.1	1.5	2.3	5.5	2.5
C_5^+ Hydrocarbons Product Distribution							
C_5 - C_8 Saturates	16.3	14.2	21.2	29.4	20.2	20.1	26.5
C_5 - C_8 Unsaturates	0.4	0.2	0.7	0.4	0.3	0.6	1.1
C_9^+ P+O+N	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.3	0.3	0.4	0.3	0.2	0.3	0.3
Toluene	1.7	1.4	1.7	1.3	1.3	1.6	1.5
C_8 Aromatics	17.2	14.0	16.2	13.9	13.5	15.2	14.0
C_9 Aromatics	38.6	36.6	36.6	32.3	33.8	34.0	32.6
C_{10} Aromatics	19.5	24.5	18.9	19.1	25.6	18.1	19.0
C_{11} Aromatics	3.9	4.2	3.0	2.7	3.8	4.7	3.4
C_{12} Aromatics	1.1	3.3	0.9	0.5	1.0	2.7	1.0
C_{13} Aromatics	1.0	1.3	0.4	0.1	0.3	2.0	0.5
C_{14} Aromatics	0.0	0.0	0.0	0.0	0.0	0.3	0.0
C_{15} Aromatics	0.0	0.0	0.0	0.0	0.0	0.4	0.1

* : Run conducted at standard operating conditions to assess activity decay.

Table 20b: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 400°C.
Catalyst: 63% $ZnO-Cr_2O_3$ (Zn/Cr 25/75), 27% HZSM-5, 10% Al_2O_3 binder.

The rate equation is:

$$r = \frac{(f_{CO} P_{CO} f_{H_2}^{2} P_{H_2}^{2} - \frac{1}{Keq} f_{CH_3OH} P_{CH_3OH})\ \exp\ (-b9.t)}{A^3\ (1 + B\ f_{CO} P_{CO} + C\ f_{H_2}\ P_{H_2} + D\ f_{CO_2}\ P_{CO_2})^3}$$

$A = b_1 \exp\ (b_2/RT)$ $\quad$ $C = b_5 \exp\ (b_6/RT)$

$B = b_3 \exp\ (b_4/RT)$ $\quad$ $D = b_7 \exp\ (b_8/RT)$

where

- f_i are the fugacity coefficients for the component i,
- P_i are the partial pressures for the component i (atm)
- Keq is the thermodynamic equilibrium constant for the methanol synthesis reaction
- t is the cumulative time on stream (min)

An exponential decay function with the time on stream was also introduced to take into account the catalyst deactivation. The activity decay of the catalyst is actually illustrated in Figure 12. This figure depicts the variation, with the time on stream, of the reation rates of CO conversion measured under identical operating conditions, for the three levels of temperature studied. The corresponding runs are marked with an "*" in Tables 15 to 20. No significant effect of the temperature on the rate of activity decay was found, in the range 355-405°C.

It has to be pointed out that data analysis could be dealt with if the reaction equilibrium term appearing in the numerator of the rate equation (backward reaction) is neglected. This assumption was supported by the fact that no methanol was detected in the products.

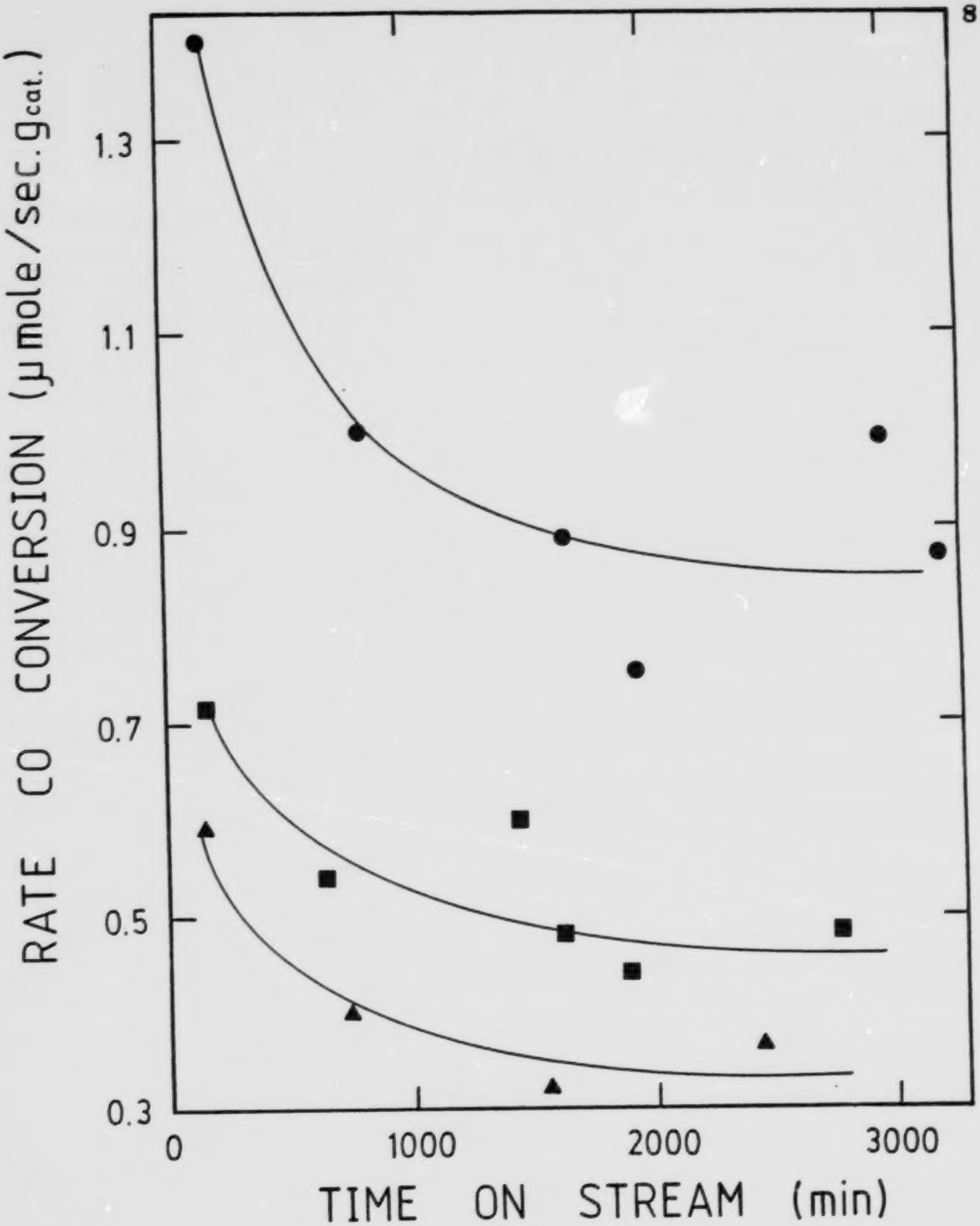


Figure 12. Variations of the rate of CO conversion with the time-on-stream, observed for the syngas conversion to hydrocarbons kinetic runs, in the Berty Reactor (●: 400°C, ■: 375°C, ▲: 355°C)

The best estimates for the b parameters are:

b_1 - 0.55 atm. (μmole/sec.g cat.)$^{-1/3}$
b_2 - 2900 (cal/mole)$^{1/3}$
b_3 - 8.25E-5 atm^{-1}
b_4 - 8600 cal/mole
b_5 - 2.79E-5 atm^{-1}
b_6 - 9130 cal/mole
b_7 - .19 atm^{-1}
b_8 - 850 cal/mole
b_9 - 3.05E-4 min^{-1}

The experimental and calculated rates of CO conversion are compared in Figure 13. The average deviation is 16%. It should be mentioned that, for the determination of the parameters, several computer parameter estimations starting with values for the initial guesses varying over a wide range were considered. The numerical regression was always converging towards the same final estimates for the 9 parameters, indication of the adequacy of the 43 kinetic runs and the numerical technique adopted.

Consequently, this rate equation was considered appropriate and was used in this research for the simulation of the runs conducted in the pilot unit reactor.

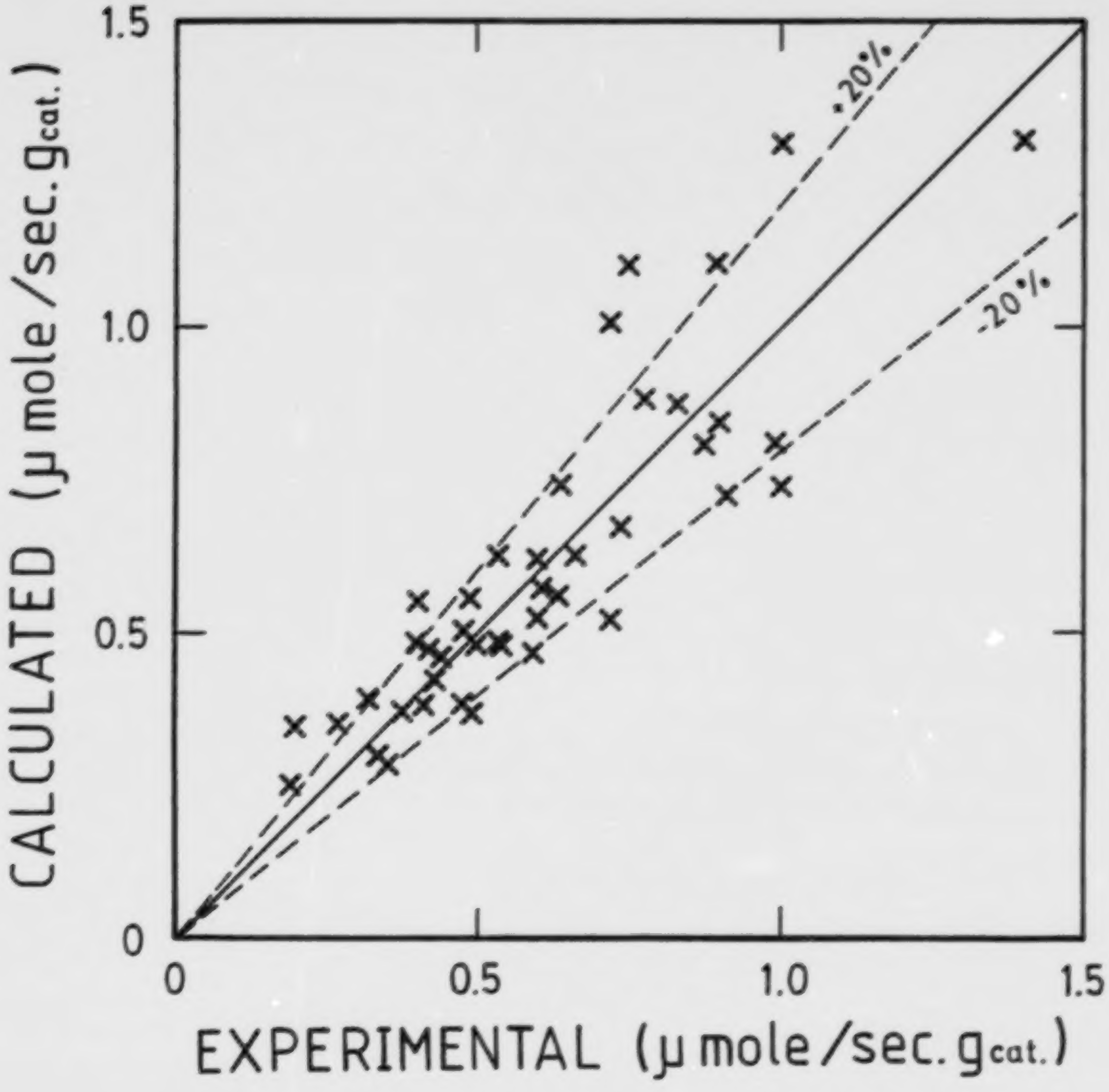


Figure 13: Comparaison of Experimental and Calculated CO Conversion Rates in the Direct Conversion of Syngas to Hydrocarbons Kinetic Runs in the Berty Reactor.

C. CANMET Catalysts

The Berty Reactor set-up and analytical procedures described in the previous section was used for the kinetic study of syngas conversion on the two catalysts # 102 and 112.

CANMET Catalyst Code # 102

Following the instructions given by Dr. I Galuszka from CANMET, 10 grams of the sample were mixed with 2% wt. of stearic acid as a lubricant aid, and compressed under 16000 psig into a 1" 1/4 pellet. This pellet was broken into granules with a 1/8" average size. The stearic acid was burned off in air by rising slowly the temperature of the calcination up to 400°C. The sample was kept at this temperature for 16 hours. Then, the catalyst was prereduced in the reactor by circulating pure H_2 (1 atm, 400°C, for 24 hours).

Following this pretreatment, the reacting system was kept under helium circulation at 300°C for 16 hours then, brought to the typical reaction conditions: 220 psig, 300°C, H2/CO = 1 and, a WHSV of 590 ml STP/g cat./hr. The reaction was carried on for 6 days, 24 hours a day, the reactor stirring shaft being shut off during the night. No activity for the conversion of the synthetic gas mixture was observed during that period of time. This result was reported to Dr. Galuszka and no explanation could be found for this absence of activity, at the present time. Consequently, with Dr. Galuszka's agreement, the reaction test for this catalyst sample was terminated.

The spent catalyst sample displayed the typical grey colour which could be the result of the presence of the iron in its reduced state (iron carbides or metal iron) or the presence of carbon deposits, the first case being more plausible given the fact that no activity was observed from the beginning of the reaction test. Samples of the fresh and the spent catalyst will be sent to CANMET.

CANMET Catalyst Code # 112

This catalyst sample has a much lighter texture that the sample # 102, and was much more difficult to pelletize. Water was added to the catalyst to form a paste, making the pelletization possible. No stearic acid was incorporated, in this case. After drying at 110°C, the pellet was broken into granules with sizes ranging between 1/8" and 1/4". The catalyst sample was pretreated according to the same procedure used for the CANMET catalyst #102, with the exception that pure H_2 was replaced by a 7.8% H_2 in helium mixture for the prereduction step.

10.9 g of catalyst were tested under the same conditions used for the sample #102. Activity was observed from the beginning of the run. The conversion increased slowly to reach a constant level after around 100 hours of time of stream. No sensible variation in the product distribution was observed during that period. The steady-state CO conversion reached was 32-33%. CO_2 was observed in the products, revealing an important water gas shift activity. Methane amounts to around 30% of the hydrocarbon formed, C_2 to 16%, C_3 to 19%, C_4 to 13.5% and C_5-C_{12} to 19%. At this stage, the systematic kinetic runs were initiated.

Twenty-eight (28) kinetic runs for the catalytic study of the syngas conversion to hydrocarbons over the catalyst CANMET #112 were performed, as part of the program. Three series of runs, at three different temperatures, 270°C, 300°C and 330°C were conducted. The same batch of catalyst (mass of 10.9g) was used for the three series of runs. Between each kinetic run, the catalyst was maintained in the reactor under a 30 ml/min syngas flow, at the temperature, pressure and H_2/CO ratio identical to those of the last run carried on. However, the stirring shaft was shutt off during the nights. The alternative would have been to keep the catalyst sample under an inert helium gas flow when no kinetic data were collected. This was not found convenient, however, because of the long period of time required for reaching the steady-state when the feed was switched back to the syngas mixture. As a consequence, the cumulative time-on-stream reported for each run includes the period of time between each run.

The operating conditions for each run were a combination of the following values:

- for the pressure: 220, 300, 400 psig
- for the WHSV : 190, 315, 475, 1240 ml STP/g_{cat}/hr
- for H_2/CO : 1, 2.

The overall procedure for data collection and mathematical processing was similar to the one applied for the kinetic study of the syngas conversion via the methanol route, described in the previous section. This procedure was actually simplified by the fact that only water was condensed and, as a result no analysis of a liquid hydrocarbon phase was required. Indeed, as indicated by the hydrocarbon product distribution, some C_5^+ hydrocarbons are formed, although not in a sufficient amount over the two to four hours period for a typical run, to form a distinctive liquid phase. The computer program for the calculation of conversions, mass balances and product distribution is identical to SGPROD, the program used in the study of syngas conversion over the ZnO-Cr_2O_3-HZSM-5 catalyst, except regarding the definition of the lumped species. A copy of the result printout is given in Appendix F.

Run operating conditions, conversions, product distributions and mass balances are reported in Tables 21 to 26. In order to assess the catalyst deactivation, a run was carried out at regular intervals, at the following conditions: 300°C, 16 atm, WHSV 475-480 ml STP/g_{cat}/hr, H_2/CO 1.0 . The results for these runs are gathered in Tables 27 and 28. As shown in these tables, the CO and H_2 conversions decreased respectively, from 32% to 22%, and from 39% to 26.6%, over a cumulative time-on-stream of 844 hours. The WGS activity was found to decrease as well, as indicated by the CO_2 fraction in the products. The selectivity to the C_1 and C_2 fractions was rising as the catalyst activity was decaying.

Mass balances were closed within 5%. CO and H_2 conversions were ranging repectively, from 5% to 46%, and 6% to 48%.

The catalyst displayed the behaviour usually observed for typical Fischer-Tropsch catalysts:

- higher selectivity to C_1 and C_2 hydrocarbons was observed when the temperature was risen, while olefins selectivity decreased;

RUN #	880728A	880729A	880802A	880803A	880804A	880805A
OPERATING CONDITIONS						
Temperature (°C)	300.00	298.00	297.00	299.00	299.00	299.00
Pressure (atm.)	16.00	16.00	21.10	21.40	21.10	21.10
H_2/CO molar	0.99	0.97	0.95	0.98	0.99	1.00
Feed Flowrate (mole/sec)	60.50	155.10	60.10	155.00	23.50	39.30
WHSV (ml STP/g_{cat}/hr)	484.00	1240.00	480.00	1239.00	188.00	314.00
Test Duration (min)	394.00	362.00	460.00	363.00	366.00	152.00
Cum. Time on stream (hrs)	150.00	174.00	270.00	294.00	318.00	342.00
CONVERSIONS						
H_2	37.9	21.4	44.3	23.6	62.3	43.3
CO	32.0	15.0	37.6	16.6	61.2	37.8
PRODUCT MASS DISTRIBUTION						
CO_2	53.6	45.3	54.5	42.5	63.5	58.7
H_2O	14.5	22.6	13.8	23.4	6.6	10.5
Hydrocarbons	31.9	32.1	31.7	34.1	29.9	30.8
Oxygenates	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)						
C	1.0	-0.3	-2.7	0.7	-6.6	3.6
H	0.0	-0.7	-1.7	0.0	-4.3	0.0
O	-0.2	0.3	-4.0	-0.8	-9.5	2.1
TOTAL	0.3	0.0	-3.2	-0.8	-6.6	2.7
CHAIN GROWTH PROBABILITY						
α	0.48	0.47	0.48	0.46	0.45	0.45

Table 21a: Results of the syngas conversion kinetic runs in the Berty Reactor at 300°C.
Catalyst: CANMET #112.

RUN #	880809A	880809B	880810A	880810B	880825B
OPERATING CONDITIONS					
Temperature (°C)	299.00	301.00	300.00	301.00	300.00
Pressure (atm.)	16.00	21.10	27.90	28.20	16.00
H_2/CO molar	2.10	2.08	1.96	1.88	2.16
Feed Flowrate (mole/sec)	59.60	58.70	58.90	152.90	40.30
WHSV (ml STP/g_{cat}/hr)	476.00	469.00	471.00	1222.00	322.00
Test Duration (min)	210.00	181.00	264.00	159.00	185.00
Cum. Time on stream (hrs)	436.00	440.00	459.00	464.00	825.00
CONVERSIONS					
H_2	20.0	25.1	29.8	15.4	39.6
CO	25.1	32.6	38.7	20.6	58.6
PRODUCT MASS DISTRIBUTION					
CO_2	43.4	45.1	44.4	37.6	52.4
H_2O	22.4	19.8	18.5	25.2	14.1
Hydrocarbons	34.2	35.1	37.1	37.2	33.5
Oxygenates	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)					
C	-0.8	-3.5	1.7	-0.6	3.0
H	-1.2	-3.8	0.0	2.0	0.0
O	-0.7	-4.9	-2.8	-1.6	-0.6
TOTAL	-0.8	-3.1	-0.9	-0.7	1.0
CHAIN GROWTH PROBABILITY					
α	0.33	0.35	0.36	0.35	0.42

Table 21b: Results of the syngas conversion kinetic runs in the Berty Reactor at 300°C.
Catalyst: CANMET #112.

RUN #	880728A	880729A	880802A	880803A	880804A	880805A
C_1	31.3	33.5	32.1	34.7	37.9	37.7
C_2	16.6	17.0	16.7	16.5	19.5	19.0
% $C_2^=$ in C_2	10.2	17.2	7.3	11.7	3.2	4.5
C_3	20.0	20.0	18.8	17.8	18.8	18.3
% $C_3^=$ in C_3	48.0	60.4	39.4	51.6	16.8	22.8
C_4	13.3	10.4	13.7	13.7	10.6	11.3
% $C_4^=$ in C_4	62.1	91.1	52.1	56.4	33.6	39.5
C_5	9.2	8.9	8.9	8.4	6.6	6.9
% $C_5^=$ in C_5	56.2	62.9	49.3	53.2	38.6	39.6
C_6	5.2	5.4	4.8	4.6	3.4	3.5
% $C_6^=$ in C_6	56.3	58.2	51.0	53.2	35.4	42.1
C_7	1.5	2.3	2.3	2.1	1.5	1.6
C_8	1.3	1.2	1.2	1.2	0.79	0.78
C_9	0.64	0.49	0.59	0.44	0.37	0.37
C_{10}	0.32	0.24	0.29	0.24	0.23	0.24
C_{11}	0.20	0.18	0.19	0.16	0.10	0.12
C_{12}	0.13	0.13	0.13	0.13	0.07	0.08
C_{13}	0.09	0.10	0.09	0.09	0.05	0.06
C_{14}	0.07	0.07	0.07	0.07	0.04	0.05
C_{15}	0.05	0.06	0.04	0.05	0.04	0.03
C_{16}	0.05	0.05	0.04	0.03	0.03	0.03

Table 22a: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 300°C.
Catalyst: CANMET #112.

RUN #	880809A	880809B	880810A	880810B	880825B
C_1	58.3	56.5	54.6	53.2	58.2
C_2	18.1	18.8	17.5	17.9	18.4
% $C_2^=$ in C_2	2.5	5.3	-	5.9	0.5
C_3	11.8	12.1	12.4	12.2	11.9
% $C_3^=$ in C_3	21.1	20.8	16.1	26.6	5.5
C_4	7.0	7.6	9.2	10.2	6.1
% $C_4^=$ in C_4	30.3	24.8	27.1	31.1	22.9
C_5	2.7	2.8	3.8	4.4	2.5
% $C_5^=$ in C_5	32.3	26.1	26.1	29.1	28.6
C_6	0.91	1.0	1.3	1.1	1.3
% $C_6^=$ in C_6	23.1	27.0	38.8	29.2	9.2
C_7	0.35	0.49	0.55	0.53	0.72
C_8	0.17	0.24	0.23	0.17	0.40
C_9	0.09	0.10	0.10	0.09	0.21
C_{10}	0.05	0.11	0.09	0.06	0.14
C_{11}	0.04	0.03	0.04	0.04	0.07
C_{12}	0.03	0.03	0.03	0.03	0.04
C_{13}	0.00	0.02	0.02	0.02	0.03
C_{14}	0.15	0.11	0.09	0.07	0.05
C_{15}	0.30	0.00	0.02	0.02	0.02
C_{16}	0.06	0.01	0.01	0.01	0.05

Table 22b: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 300°C.
Catalyst: CANMET #112.

RUN #	880812A	880812B	880815A	880815B	880816A	880817A
OPERATING CONDITIONS						
Temperature (°C)	270.00	272.00	269.00	269.00	270.00	271.00
Pressure (atm.)	16.30	16.30	16.00	20.70	28.20	16.30
H_2/CO molar	0.96	0.97	0.99	1.00	1.01	1.01
Feed Flowrate (mole/sec)	155.80	60.00	38.80	40.60	40.80	39.70
WHSV (ml STP/g_{cat}/hr)	1245.00	479.00	310.00	324.00	326.00	317.00
Test Duration (min)	277.00	142.00	147.00	176.00	206.00	329.00
Cum. Time on stream (hrs)	507.00	512.00	579.00	583.00	606.00	629.00
CONVERSIONS						
H_2	5.9	11.5	13.3	18.1	25.8	14.6
CO	4.4	8.0	8.2	10.4	10.5	8.5
PRODUCT MASS DISTRIBUTION						
CO_2	35.4	36.1	40.5	39.7	38.5	39.2
H_2O	40.2	29.3	22.9	23.9	23.0	26.8
Hydrocarbons	24.4	34.6	36.6	36.4	38.5	34.4
Oxygenates	0.0	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)						
C	-2.1	-1.8	3.1	1.0	3.0	0.8
H	-0.7	0.0	2.6	0.0	-4.9	0.0
O	-0.7	-1.6	2.2	0.3	1.3	1.1
TOTAL	-1.3	-1.7	2.3	0.6	1.2	0.9
CHAIN GROWTH PROBABILITY						
α	0.45	0.48	0.50	0.49	0.49	0.49

Table 23a: Results of the syngas conversion kinetic runs in the Berty Reactor at 270°C.
Catalyst: CANMET #112.

RUN #	880818A	880819A	880825A
OPERATING CONDITIONS			
Temperature (°C)	271.00	270.00	269.00
Pressure (atm.)	21.40	28.20	28.20
H_2/CO molar	2.01	1.86	2.11
Feed Flowrate (mole/sec)	39.30	39.80	60.70
WHSV (ml STP/g_{cat}/hr)	314.00	318.00	485.00
Test Duration (min)	167.00	175.00	158.00
Cum. Time on stream (hrs)	652.00	676.00	820.00
CONVERSIONS			
H_2	19.2	20.5	20.4
CO	22.0	26.8	23.7
PRODUCT MASS DISTRIBUTION			
CO_2	35.2	33.3	30.4
H_2O	24.9	25.6	39.3
Hydrocarbons	39.9	41.1	30.3
Oxygenates	0.0	0.0	0.0
MASS BALANCE (%)			
C	-4.2	-7.3	-4.2
H	-3.8	-1.9	-1.2
O	-6.5	-10.0	2.2
TOTAL	-3.9	-7.4	-0.6
CHAIN GROWTH PROBABILITY			
α	0.45	0.45	0.43

Table 23b: Results of the syngas conversion kinetic runs in the Berty Reactor at 270°C.
Catalyst: CANMET #112.

RUN #	880812A	880812B	880815A	880815B	880816A	880817A
C_1	37.6	34.3	31.7	32.7	30.2	36.0
C_2	18.4	18.3	16.6	16.7	15.7	15.2
% $C_2^=$ in C_2	23.3	12.2	-	9.0	8.7	9.8
C_3	17.4	16.4	17.2	17.3	17.0	18.0
% $C_3^=$ in C_3	66.0	51.2	43.5	42.5	44.9	45.3
C_4	12.7	14.9	15.9	14.0	17.1	9.0
% $C_4^=$ in C_4	71.7	53.5	47.8	45.7	44.5	73.3
C_5	5.8	7.8	9.0	9.2	9.7	9.1
% $C_5^=$ in C_5	59.5	54.0	45.3	44.6	40.2	44.8
C_6	3.4	3.6	4.1	4.8	5.2	4.8
% $C_6^=$ in C_6	51.2	45.1	44.9	53.0	54.5	51.7
C_7	2.1	1.8	2.2	2.4	2.4	2.1
C_8	1.0	1.1	1.2	1.3	1.3	1.2
C_9	0.39	0.48	0.70	0.68	0.62	0.60
C_{10}	0.22	0.37	0.45	0.15	0.10	0.38
C_{11}	0.19	0.19	0.27	0.25	0.25	0.22
C_{12}	0.17	0.15	0.20	0.18	0.18	0.16
C_{13}	0.14	0.12	0.15	0.13	0.13	0.11
C_{14}	0.49	0.21	0.17	0.15	0.14	0.17
C_{15}	0.09	0.07	0.11	0.08	0.08	0.07
C_{16}	0.11	0.07	0.11	0.02	0.08	0.07

Table 24a: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 270°C.
Catalyst: CANMET #112.

RUN #	880818A	880819A	880825A
C_1	44.0	44.1	47.7
C_2	15.9	15.8	19.4
% $C_2^=$ in C_2	-	-	7.7
C_3	14.5	14.4	14.6
% $C_3^=$ in C_3	22.0	21.7	19.9
C_4	12.6	13.53	9.6
% $C_4^=$ in C_4	24.9	22.2	25.8
C_5	6.7	7.1	4.1
% $C_5^=$ in C_5	26.9	26.3	38.3
C_6	3.2	2.3	2.10
% $C_6^=$ in C_6	46.7	30.9	25.7
C_7	1.3	1.3	0.95
C_8	0.66	0.61	0.63
C_9	0.33	0.32	0.25
C_{10}	0.22	0.20	0.20
C_{11}	0.11	0.10	0.10
C_{12}	0.08	0.07	0.08
C_{13}	0.05	0.05	0.07
C_{14}	0.08	0.07	0.14
C_{15}	0.02	0.04	0.09
C_{16}	0.06	0.04	0.12

Table 24b: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor at 270°C.
Catalyst: CANMET #112.

RUN #	880826B	880829A	880829B	880830A
OPERATING CONDITIONS				
Temperature (°C)	332.00	328.00	330.00	229.00
Pressure (atm.)	16.60	16.00	16.00	21.40
H_2/CO molar	1.03	1.03	0.99	1.03
Feed Flowrate (mole/sec)	60.70	155.40	39.50	59.60
WHSV (ml STP/g_{cat}/hr)	485.00	1242.00	315.00	477.00
Test Duration (min)	184.00	150.00	206.00	211.00
Cum. Time on stream (hrs)	849.00	916.00	919.00	940.00
CONVERSIONS				
H_2	46.0	23.1	47.8	46.8
CO	42.2	17.4	45.6	40.7
PRODUCT MASS DISTRIBUTION				
CO_2	61.7	50.3	61.9	60.5
H_2O	10.2	25.3	10.0	12.1
Hydrocarbons	28.1	24.4	28.1	27.4
Oxygenates	0.0	0.0	0.0	0.0
MASS BALANCE (%)				
C	-0.9	-2.4	-6.4	-2.4
H	0.0	-1.3	-2.5	-3.3
O	0.9	2.8	-4.8	0.8
TOTAL	0.1	0.4	-4.8	-0.7
CHAIN GROWTH PROBABILITY				
α	0.40	0.36	0.41	0.39

Table 25: Results of the syngas conversion kinetic runs in the Berty Reactor at 330°C.
Catalyst: CANMET #112.

RUN #	880826B	880829A	880829B	880830A
C_1	55.2	54.9	54.4	52.5
C_2	21.3	20.4	21.1	20.5
% $C_2^=$ in C_2	2.2	13.2	3.0	2.8
C_3	15.3	13.6	15.3	14.9
% $C_3^=$ in C_3	15.3	46.8	21.8	19.2
C_4	2.4	6.0	3.1	6.4
% $C_4^=$ in C_4	98.7	61.9	98.4	35.1
C_5	3.1	2.7	3.1	3.1
% $C_5^=$ in C_5	44.0	62.8	51.9	47.9
C_6	1.4	1.2	1.5	1.4
% $C_6^=$ in C_6	26.1	46.6	36.6	31.9
C_7	0.62	0.63	0.71	0.58
C_8	0.35	0.27	0.32	0.28
C_9	0.16	0.07	0.16	0.14
C_{10}	0.11	0.04	0.13	0.08
C_{11}	0.04	0.03	0.04	0.03
C_{12}	0.03	0.02	0.02	0.02
C_{13}	0.02	0.02	0.02	0.01
C_{14}	0.03	0.06	0.04	0.03
C_{15}	0.01	0.03	0.01	0.03
C_{16}	0.01	0.03	0.05	0.02

Table 26: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs
in the Berty Reactor at 330°C.
Catalyst: CANMET #112.

RUN #	880728A	880805B	880811A	880816B	880826A
OPERATING CONDITIONS					
Temperature (°C)	300.00	300.00	299.00	302.00	299.00
Pressure (atm.)	16.00	16.00	16.70	16.30	16.00
H_2/CO molar	0.99	0.99	0.97	0.93	1.02
Feed Flowrate (mole/sec)	60.50	59.40	60.30	59.40	59.40
WHSV (ml STP/g_{cat}/hr)	484.00	475.00	482.00	474.00	474.00
Test Duration (min)	394.00	227.00	316.00	151.00	151.00
Cum. Time on stream (hrs)	150.00	345.00	483.00	611.00	844.00
CONVERSIONS					
H_2	37.9	30.8	28.6	38.5	26.6
CO	32.0	23.2	21.1	25.4	22.0
PRODUCT MASS DISTRIBUTION					
CO_2	53.6	52.2	50.5	51.9	48.9
H_2O	14.5	15.1	16.1	14.6	24.1
Hydrocarbons	31.9	32.7	33.4	33.5	27.0
Oxygenates	0.0	0.0	0.0	0.0	0.0
MASS BALANCE (%)					
C	1.0	1.7	-0.3	2.4	-2.9
H	0.0	0.0	0.0	0.0	0.0
O	-0.2	0.6	-1.3	0.5	1.6
TOTAL	0.3	1.1	0.9	1.3	-0.3
CHAIN GROWTH PROBABILITY					
α	0.48	0.45	0.45	0.48	0.42

Table 27: Results of the syngas conversion kinetic runs in the Berty Reactor, conducted under fixed conditions to assess the deactivation with time-on-stream. Catalyst: CANMET #112.

RUN #	880728A	880805B	880811A	880816B	880826A
C_1	31.3	38.1	40.9	37.2	47.7
C_2	16.6	18.3	19.5	19.4	20.6
% $C_2^=$ in C_2	10.2	4.2	7.3	7.4	6.9
C_3	20.0	18.2	16.7	17.6	15.9
% $C_3^=$ in C_3	48.0	32.4	34.0	31.9	29.7
C_4	13.3	11.9	10.5	11.7	8.0
% $C_4^=$ in C_4	62.1	47.0	44.6	43.3	44.5
C_5	9.2	6.9	6.4	6.5	3.9
% $C_5^=$ in C_5	56.2	46.1	44.0	46.8	53.2
C_6	5.2	3.5	3.0	3.4	1.8
% $C_6^=$ in C_6	56.3	44.6	49.8	41.8	36.5
C_7	1.50	1.50	1.30	1.70	0.89
C_8	1.30	0.77	0.72	1.00	0.48
C_9	0.64	0.31	0.37	0.49	0.18
C_{10}	0.32	0.22	0.22	0.33	0.15
C_{11}	0.20	0.11	0.11	0.19	0.07
C_{12}	0.13	0.07	0.07	0.13	0.05
C_{13}	0.09	0.05	0.05	0.09	0.04
C_{14}	0.07	0.05	0.08	0.09	0.09
C_{15}	0.05	0.03	0.03	0.06	0.03
C_{16}	0.05	0.03	0.03	0.05	0.03

Table 28: Hydrocarbon Product Distributions for the Syngas Conversion Kinetic Runs in the Berty Reactor, conducted under fixed conditions to assess the deactivation with time-on-stream.
Catalyst: CANMET #112.

- the conversion was enhanced by higher pressure, while the product distribution was barely affected;
- shorter contact time (higher WHSV) favored olefins production;
- an increase of the H_2/CO ratio resulted in more methane and less olefins in the products.

Schulz-Flory-Anderson Product Distribution.

In the Fischer-Tropsch reaction on conventional catalysts, it has been established that the carbon number product distribution obeys the following relation.

$$\log (W_n/n) = n \log\alpha + \log [(1- \alpha)^2/\alpha]$$

where W_n is the mass fraction of the hydrocarbons with n carbons, and α the probability of chain growth, assumed to be independant of the hydrocarbon chain length.

This equation was applied to the data of each run presented in this report, using a computer program SCHULZ. A copy of this program is given in Appendix G. In accordance with the formulation of the equation, the calculated values of $\log(W_n/n)$ were plotted against the corresponding values of the carbon number n. Then, a linear regression was employed to calculate the slope $\log\alpha$ of the linear function. The plots for each run are reproduced in Appendix G. As shown, the Schulz-Flory-Anderson model predicts adequately the product distribution of hydrocarbons with a carbon number up to 9 to 12, but does not apply at higher carbon numbers n. However, the hydrocarbons with a chain length of more than

9 or 10 carbons were found in very low concentrations in the products and, as a consequence, were determined with an unsufficient accuracy (see tables 22a-b, 24a-b, 26 and 28) to include those components in the Schulz-Flory-Anderson product distribution.

The calculated chain growth probabilities, α, are reported in the tables 21a-b, 23a-b, 25 and 27, with the operating conditions of each run. The values varied over a relatively short range, 0.35 to 0.50. No significant or consistent effect of the pressure or the space velocity on the chain growth probability was detected, over the range of conditions studied. On the contrary, the temperature of the reaction seems to affect the chain growth probability, the α values decreasing from 0.45-0.50 down to 0.36-0.41 when the temperature was raised from 270°C to 330°C. An increase of the H_2 partial pressure favors as well the chain growth termination as the α values were found to decrease from 0.48-0.50 down to 0.43-0.45 at 270°C, and from 0.45-0.48 down to 0.33-0.42 at 300°C, when the H_2/CO ratio in the feed was increased from 1 to 2.

SECTION IV

Pseudoadiabatic Reactor Tests

IV. Pseudoadiabatic reactor tests.

A. Introduction

The pilot plant used in this project is similar to the unit already developed in the Chemical Reactor Engineering Center laboratories for the MTG reaction (Ravella, 1987). The modification was made to adapt the reactor used previously for handling a CO, H_2 mixture at high temperature (400°C) and high pressure (50000 KPa or 750 psig).

Figure 14 shows a simplified flow plan of the reactant-product side of the equipment. The gas feeding section consists of two mass flow controllers (Brooks 5850 series) which are connected to CO and H_2 gas cylinders. This configuration allows to adjust, for the different reaction conditions, the CO/H_2 ratio as well as the total flow. To avoid back flow of the gas, check valves were installed in the circuit following the two flowmeters.

Moreover and to avoid contamination of the reactant by iron carbonyl compounds coming from the CO tank, fixed bed traps were installed before the CO mass flowmeter. These traps were filled with molecular sieves particles cylinders, of approximatively 1/16 inch, and were kept at 200°C during the experimental runs.

The two gas lines were connected to a single line going to the reactor. The inlet temperature of the gas fed to the reactor was fixed by means of a preheating section in the inlet line.

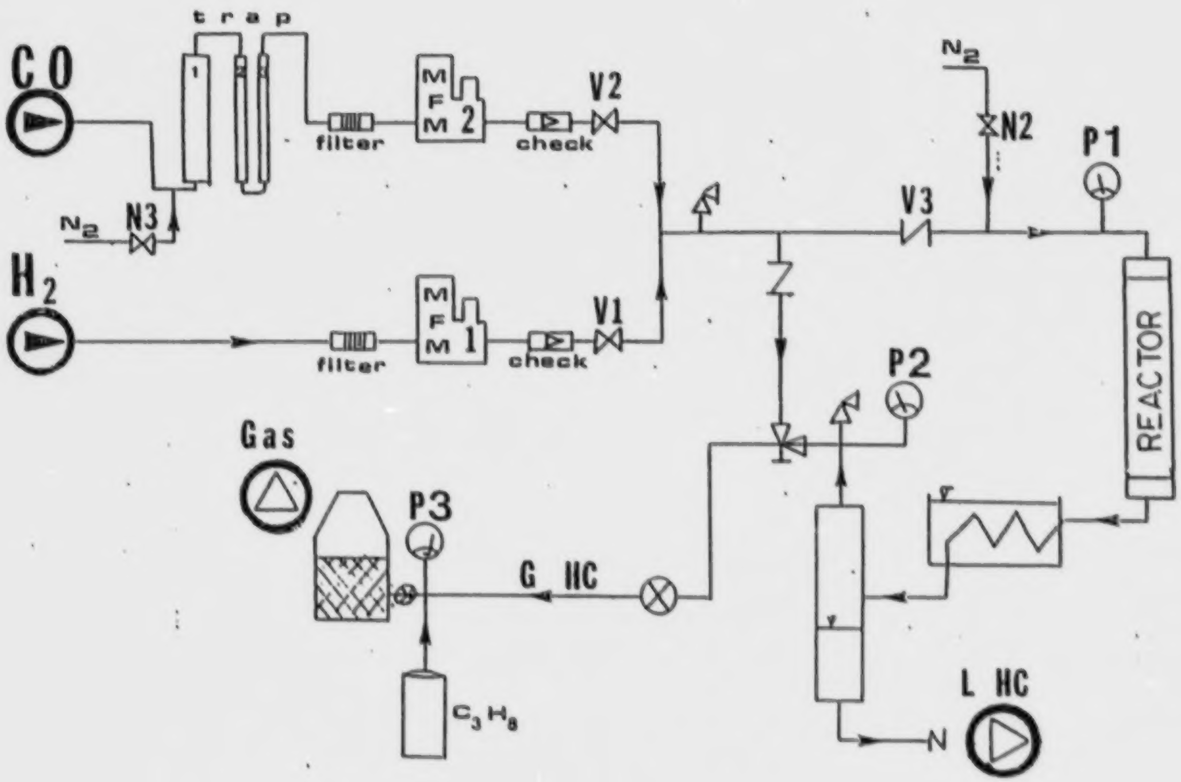

C O
t r a p
filter
M F M 2
check
V2
N2
N3
H2
filter
M F M 1
check
V1
V3
N2
N2
P1
REACTOR
P2
Gas
P3
G HC
C3H8
N
L HC

Figure 14: Simplified Flow Plan of the Pseudoadiabatic Reactor (gas side).

The circulation of the reactancts inside the reactor was down flow. This secures a better flow pattern and reactant distribution. The reaction products were condensed and then both liquid and uncondensed gases were separated. The pressure in the system was controlled by a back pressure control valve (GO inc., Model 102795, 0-500 psia) placed after the separator. Furthermore, the reactor inlet and outlet tube was provided with a pressure gauge to assess the pressure before and after the catalytic bed.

The uncondensed gases leaving the product separator were burned in a catalytic gas burner (Coleman, model 5447-901). This burner is based on the use of a Pt impregnated ceramic fiber cloth.

To perform a mass balance in the unit, essential information like inlet flow and composition were needed. In order to obtain these data, a bypass line was installed between the reactor inlet and the reactor outlet. This bypass line permitted also, before the beginning of each run, a fine adjustement of flows and relative concentrations of both carbon monoxide and hydrogen.

A general diagram of the cooling system is presented in Figure 15. It has to be pointed out that the coolant loop for the pilot plant was described in detail by Ravella (1987). We are going to describe here only the characteristics of the main components. The coolant fluid is pumped from a storage tank to the top of the reactor, co-currently with the feed. The coolant leaving the reactor is sent in turn to a second storage tank, from where it could be returned to the feeding tank by gravity. The inlet coolant temperature was fixed in each one of the runs by means of a preheating section in the inlet line. In the present study, the heat transfer fluid used was Therminol 75 manufactured

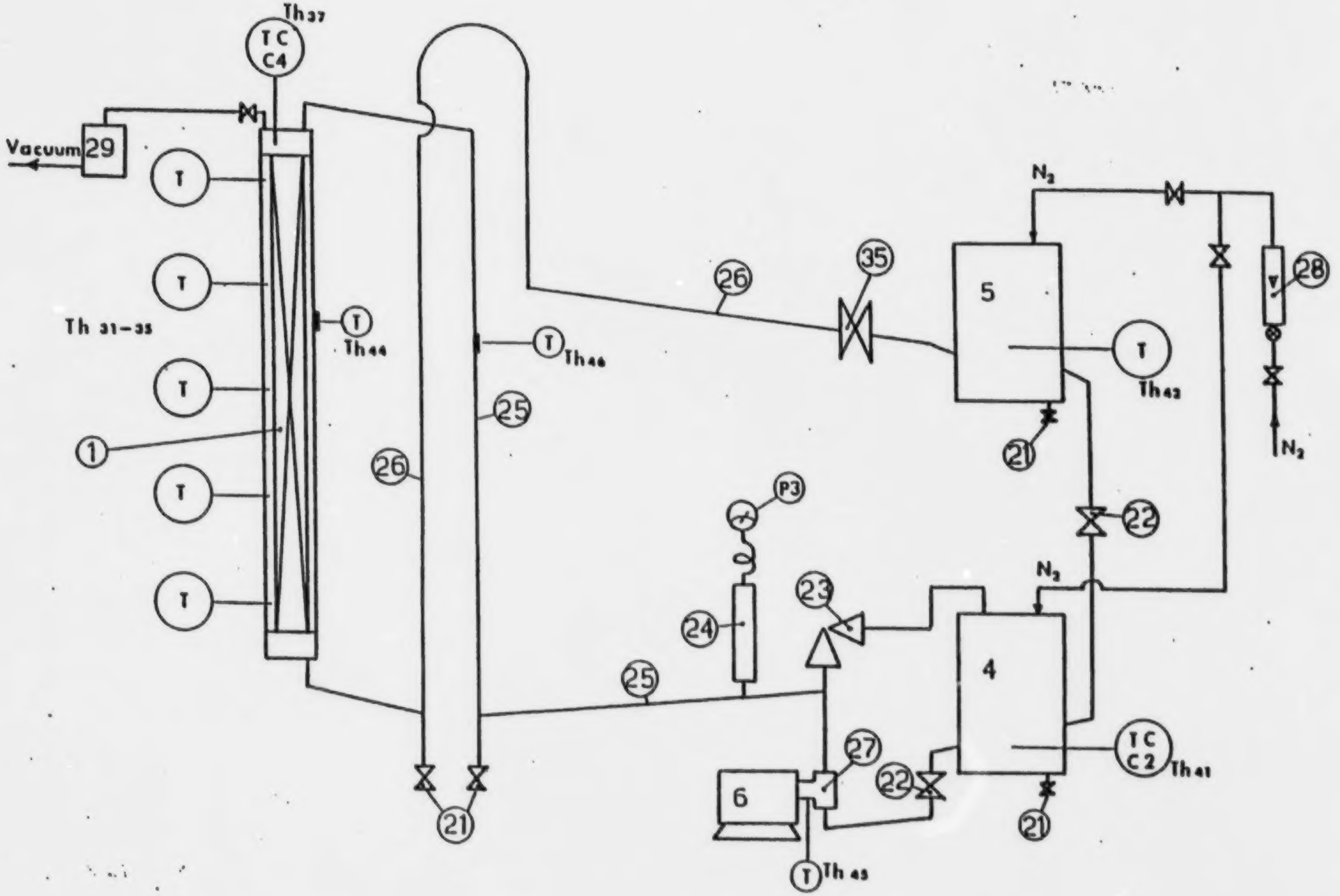

Th37
TC
C4
Vacuum
29
T
T
T
T
T
Th 31-35
1
T
Th44
26
T
Th46
25
26
21
35
5
T
Th42
21
N2
N2
28
22
N2
P3
24
23
25
4
TC
C2
Th41
6
27
22
21
T
Th45

Figure 15: Simplified Flow Plan of the Pseudoadiabatic Reactor
(coolant side).

by Monsanto which show convenient characteristics at the operating conditions selected: 350-390°C, 1 atm (in coolant loop).

The heaters used for the carbonyl traps, the feed inlet and the coolant inlet to the reactor were insulated Samox flexible heating tapes from Thermolyne. The power provided to the heaters were controlled by automatic Omega 2000 temperature controllers with double set point (actual set and upper limit alarm).

B. Reactor description

The new reactor for the conversion of synthesis gas is similar, in the design, to the unit already existing in our laboratories for methanol conversion. However, the new unit was specially rebuilt for operation at temperatures up to 400°C and pressures up to 50000 KPa (certified and approved high pressure unit). The reactor was also approved for critical service (i.e. for use with CO and H_2) and was made out of Stainless Steel Type 304SS.

The reactor is a single-tube, 2 m long, 0.0209 m diameter (3/4 inch Schedule 40S) jacketed unit. Extreme care was taken at the design stage to avoid leaking and contacting of the reacting stream with the cooling fluid. All the junctions were welded with the arc technique in a Argon atmosphere and verified with X-ray. The reactor before delivery was pressure tested and approved by the Safety Board of Ministry of Industry.

Figure 16 shows the overall dimensions of the reactor and the position of the thermocouples in the bed. Each level at the left hand side of the Figure 16 represents a group of three thermocouples inserts, equally spaced by 120°.

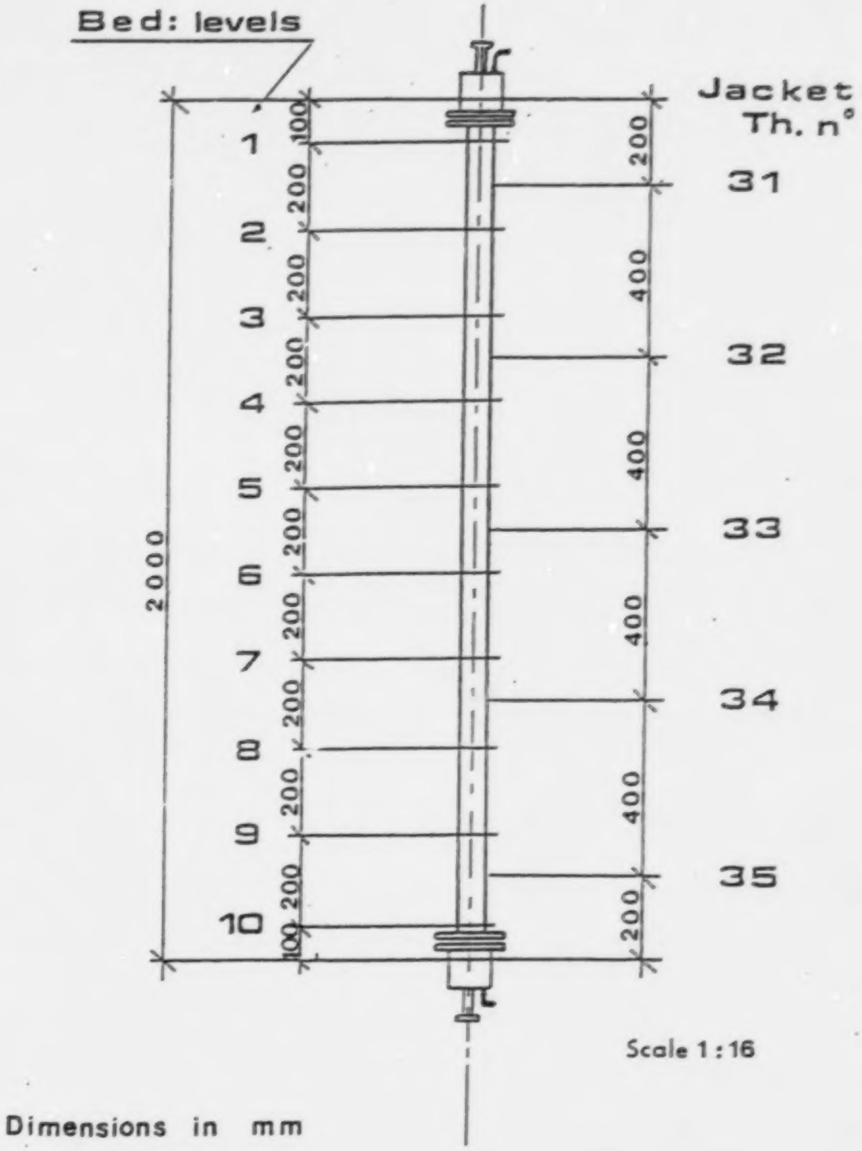

Bed: levels
Jacket Th. n°
1
2
3
4
5
6
7
8
9
10
31
32
33
34
35
2000
100
200
400
Scale 1:16
Dimensions in mm

Figure 16: Overall Dimensions of the Pseudoadiabatic Reactor.

These three thermocouples measured the temperature at three radial positions: at the center of the tube, at r/R=0.5 and close to the wall. There was, therefore, a total of 30 thermocouples in the reactor gas side. The thermocouples used were 1.5 mm in diameter with Chromel-Alumel junction, grounded type, manufactured by Omega Engineering Co. (TJ-160-CASS-116-G-8).

The jacketing of the reactor was done by a concentric pipe (1-1/4 inch Schedule 40S). The gap between the two pipes, where the coolant was circulated, was filled with steel shots of 1.5 mm in diameter to improve heat transfer in the coolant side. Figure 17 shows in detail the thermocouple insert arrangement.

The temperature in the coolant jacket was measured by five thermocouples spaced 0.4 m along the unit (Figure 16). All the thermocouples were linked to special switches (Omega 2161) and read by an Omega model 2170 digital thermometer.

The reactor was equipped with electrical heating tapes for start up of the equipment. Several layers of insulation were then laid out to minimize heat losses during the operation of the setup. Two different types of insulating material were used for this purpose. The first layer, directly in contact with the heating tapes, was a tape of high-temperature ceramic fibers, 2 inches wide by 1/8 inch thick. On top of this layer, a thick blanket of soft Durablanket (TM Carborundum) was tightly wrapped around the unit. In the present configuration, the heating tapes around the reactor were regulated by means of several Powerstat voltage regulators.

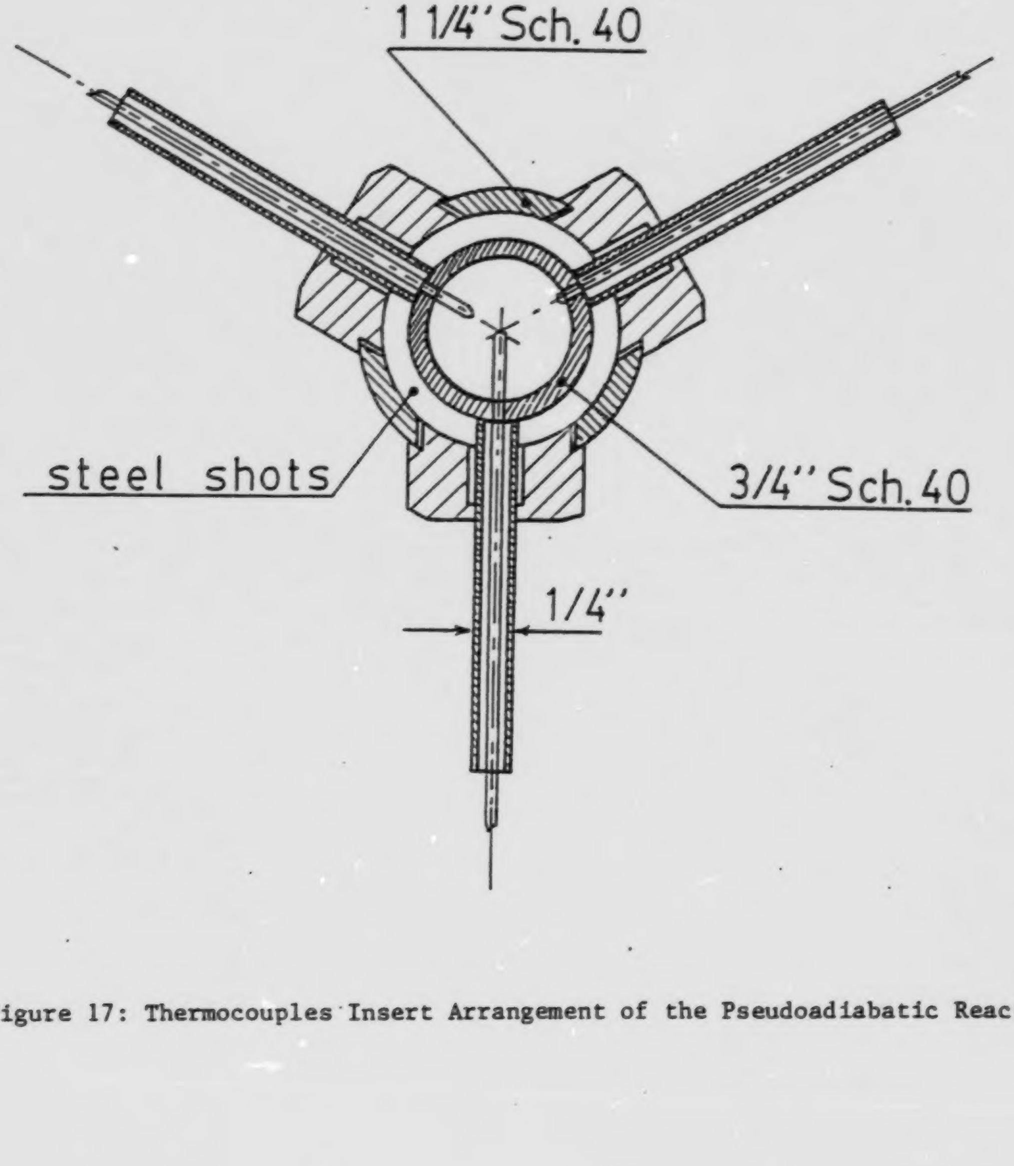

1 1/4'' Sch. 40
steel shots
3/4'' Sch. 40
1/4''

Figure 17: Thermocouples Insert Arrangement of the Pseudoadiabatic Reactor.

C. Experimental method

During each one of experiments the pilot plant unit was maintained at the selected operating temperature by means of a number of heater units with which the set up was provided. The circulation of the synthesis gas and coolant was interrupted overnight and the catalyst was kept under nitrogen atmosphere. The circulation of coolant was established a few hours before starting the flow of reactant gas. This was done in order to achieve uniform and stable temperatures along the reactor. After start-up and before feeding synthesis gas a period of usually two hours at least was allowed to reach steady-state conditions. When the temperature readings remained constant for more than half a hour, it was assumed that the pilot plant had then reached steady-state.

The synthesis gas flow and composition was fixed by means of the bypass line and a Wet Test Gas Meter (Precision Scientific G3005-3). Completed this operation, the synthesis gas was fed to the reactor.

Several temperature readings were taken during every run, at frequent time intervals. During a series of readings, a detailed data-logging sheet report was completed. In this data sheet report, uncondensed gas flows and coolant flows were also recorded.

Another important activity during each experiment was the collection of samples. Reactant gas and uncondensed gas product sample were withdrawn with a gas-tight syringe and analysed by gas chromatography. Furthermore, at the end of the run, the liquid fraction condensed was collected, weighted and finally analysed by gas chromatography. A detailed explanation of the gas chromatographic analysis was presented in section III.B.2.

Mass balances were established with three computer programs called PORDAT, PORPRO and POPROD. Listings of these program can be found in Appendix M of this report. A copy of the program printout for one of the conducted runs is also presented in Appendix H. Moreover, runs conditions, conversions and mass balances are reported in Table 29a,b,c. Total mass balances were closed within 6% which is considered as very acceptable for the type of experimental system used. Mass balances for the hydrogen were the worst ones (within 10%) and gave significant uncertainty in hydrogen conversion calculations. This was due to the difficulties in assessing hydrogen content in the outlet stream with Porapack Q chromatographic column and HWD detector.

D. Results and discussion.

A total of 19 runs were performed on the Pseudoadiabatic Catalytic Reactor. 550 g of pellets (equivalent diam.: 2.8 mm) were loaded in the reactor. The catalyst had the following composition:

- 63% Zn/Cr 25/75 at., calcined at 350°C
- 27% H-ZSM-5 Zeolite
- 10% Al_2O_3 Binder

Before the runs, the catalyst was reduced with diluted hydrogen (8% H_2 in Helium) by increasing slowly the temperature up to 300°C. It has to be mentioned that the specific methods and procedures followed for each run are described in the section IV.C.

RUN #	PO 880201	PO 880203	PO 880204	PO 880208	PO 880210	PO 880212	PO 880225	PO 880302
OPERATING CONDITIONS								
Temperature (°C)	358.20	372.20	353.70	368.70	370.90	371.30	376.30	375.50
Pressure (atm.)	34.00	34.00	34.00	34.40	20.00	34.00	34.00	34.00
Gas Flow (l/min)	16.80	3.27	3.24	5.84	2.35	3.27	16.70	16.10
Residence Time (s)	35.70	183.20	190.00	102.60	152.50	181.70	35.30	36.70
H_2/CO molar	1.05	0.96	0.96	1.06	0.96	0.96	1.04	1.04
Coolant Flow (kg/hr)	8.20	8.20	8.20	8.20	8.20	8.20	8.20	8.20
Test Duration (min)	175.00	195.00	225.00	185.00	185.00	260.00	200.00	195.00
Cum. Time on stream (hrs)	14.40	20.50	26.00	31.40	36.50	42.20	48.00	53.30
CONVERSIONS								
CO	20.6	50.3	33.1	30.5	36.2	41.2	24.1	21.6
H_2	7.8	36.1	21.6	21.2	24.2	26.4	9.4	5.8
PRODUCT MASS DISTRIBUTION								
CO_2	76.7	72.4	77.9	76.1	77.6	75.6	73.3	71.6
H_2O	1.6	0.45	0.32	0.3	0.3	1.4	2.3	3.2
Hydrocarbons	21.8	27.2	21.7	23.6	22.2	23.0	24.4	25.3
Methanol	-	-	-	-	-	-	-	Trace
MASS BALANCE (IN-OUT) (%)								
C	2.3	-3.6	-0.05	-2.5	3.2	-3.0	3.2	-0.9
H	-0.7	8.9	7.6	6.8	8.2	4.1	-1.9	-6.8
O	0.7	0.95	-2.1	-2.8	1.3	-4.9	2.9	-0.9
TOTAL	1.3	-0.38	-0.63	-2.0	2.5	-3.5	2.7	-1.3
YIELD (kg liquidHC/kgfeed)	0.0216	0.0784	0.0502	0.0453	0.0396	0.0574	0.0196	0.0239

Table 29a: Mass Balance Results

RUN #	PO 880304	PO 880307	PO 880308	PO 880309	PO 880314	PO 880316	PO 880317	PO 880318
OPERATING CONDITIONS								
Temperature (°C)	365.40	365.90	369.80	349.90	368.50	381.80	381.40	366.90
Pressure (atm.)	34.00	34.00	34.00	34.40	34.00	34.00	34.00	20.00
Gas Flow (l/min)	16.90	15.70	3.19	16.80	16.70	3.36	6.02	10.90
Residence Time (s)	35.50	38.20	188.10	36.70	35.90	175.30	98.10	32.90
H_2/CO molar	1.41	0.73	0.96	1.05	0.99	0.79	0.89	0.95
Coolant Flow (kg/hr)	8.20	8.20	8.20	8.20	16.60	8.20	8.20	8.20
Test Duration (min)	200.00	175.00	190.00	170.00	155.00	185.00	200.00	165.00
Cum. Time on stream (hrs)	58.60	63.70	68.70	73.70	78.40	83.30	88.10	92.80
CONVERSIONS								
CO	20.9	18.1	38.5	18.6	20.3	48.2	34.9	16.4
H_2	3.6	4.3	24.5	2.0	1.0	24.3	15.6	3.3
PRODUCT MASS DISTRIBUTION								
CO_2	71.3	75.2	76.0	74.2	72.6	76.4	77.5	73.2
H_2O	4.2	1.0	0.3	2.5	1.9	0.2	1.0	1.8
Hydrocarbons	24.5	23.8	23.7	23.3	25.4	23.4	21.5	25.1
Methanol	Trace	-	-	-	Trace	-	-	-
MASS BALANCE (IN-OUT) (%)								
C	2.9	4.4	-6.4	9.0	5.5	5.8	2.4	2.3
H	-3.9	-5.0	2.4	-2.6	-7.4	-1.4	-3.2	-5.0
O	2.3	4.2	-7.0	8.6	5.7	4.9	-0.5	2.4
TOTAL	1.9	3.8	-6.2	7.9	4.8	4.9	0.5	1.9
YIELD (kg liquid HC/kgfeed)	0.0156	0.0155	0.0570	0.00981	0.0137	0.0550	0.0266	0.0084

Table 29b: Mass Balance Results

RUN #	PO 880322	PO 880323	PO 880325
OPERATING CONDITIONS			
Temperature (°C)	370.00	355.50	369.90
Pressure (atm.)	34.00	34.00	34.00
Gas Flow (l/min)	3.31	6.16	3.33
Residence Time (s)	181.00	99.80	180.00
H_2/CO molar	0.81	0.88	0.96
Coolant Flow (kg/hr)	16.60	16.60	8.20
Test Duration (min)	200.00	180.00	170.00
Cum. Time on stream (hrs)	97.90	103.10	109.00
CONVERSIONS			
CO	39.2	22.7	33.3
H_2	19.9	1.3	26.0
PRODUCT MASS DISTRIBUTION			
CO_2	71.6	78.5	73.4
H_2O	2.5	2.1	1.0
Hydrocarbons	25.9	19.4	25.6
Methanol	-	-	-
MASS BALANCE (IN-OUT) (%)			
C	2.7	5.4	-7.3
H	-3.4	-7.6	5.0
O	4.0	2.6	-5.9
TOTAL	3.1	3.1	-5.7
YIELD (kg liquid HC/kgfeed)	0.0591	0.0186	0.0609

Table 29c: Mass Balance Results

Pseudoadiabatic Operating regime was studied with this group of runs changing systematically the following parameters: inlet temperature, pressure, coolant flow, residence time and H_2/CO ratio. Also, at regular periods, a given run was repeated to assess the deactivation of the catalyst.

a. Productivity

Table 30 reports the various operating conditions, conversion, liquid production and liquid yield for each test. Furthermore, Tables 31a,b,c present a typical hydrocarbon distribution observed for the products during the 19 runs. One important observation coming from Table 30 is the CO conversion level. For every test, about 12 to 17% of the CO converted go to the liquid hydrocarbon (gasoline) fraction. This conversion level value is in accordance with the stoichiometry of the combined reaction scheme for the bifunctional catalyst which includes the methanol synthesis, the MTG and the water-gas-shift reaction.

It can also be concluded from Table 30 that the liquid productivity on a per tube basis increased when temperature, pressure and flow was increased. On the other side, the yield defined as the mass of liquid hydrocarbons produced per mass of synthesis gas fed, was favoured at high residence times or the equivalent lower synthesis gas flows. This can be explained considering that when the residence time increases, the total conversion increases and consequently the amount of methanol formed and converted increases. This is achieved with a significant reduction of the partial pressure of H_2. This reduction of hydrogen partial pressure probably slows down the rate of interception of small olefins by hydrogenation and favour the oligomerization of these olefins into aromatics. As a consequence both desired factors, higher

Run	Inlet Temperature (°C) gas	coolant	Pression (atm)	Flow (l/min)	H_2/CO ratio	Coolant Flow (kg/hr)	Conversion (%) CO	H_2	Liquid Production (kg/hr)	Yield (kg/kg)	Regime
PO880201	358.2	361.3	34	16.8	1.05	8.2	20.6	7.8	0.0136	0.0216	POAT*
PO880203	372.2	372.2	34	3.3	0.96	8.2	50.3	36.1	0.0097	0.0784	POAT
PO880204	353.7	353.7	34	3.2	0.96	8.2	33.1	21.6	0.0062	0.0502	POAT
PO880208	368.7	368.7	34	5.8	1.06	8.2	30.5	21.2	0.0096	0.0453	MFARD**
PO880210	370.9	370.9	20	2.4	0.96	8.2	36.2	24.2	0.0035	0.0396	POAT
PO880212	371.3	371.3	34	3.3	0.96	8.2	41.2	26.4	0.0068	0.0574	POAT
PO880225	376.3	376.4	34	16.7	1.04	8.2	24.1	9.4	0.0119	0.0196	POAT
PO880302	375.5	376.6	34	16.1	1.04	8.2	21.6	5.8	0.0141	0.0239	POAT
PO880304	365.4	366.0	34	16.9	1.41	8.2	20.9	3.6	0.0083	0.0156	POAT
PO880307	365.9	367.6	34	15.7	0.73	8.2	18.1	4.3	0.0102	0.0155	POAT
PO880308	369.8	369.8	34	3.2	0.96	8.2	38.5	24.5	0.0069	0.0570	POAT
PO880309	349.9	351.2	34	16.8	1.05	8.2	18.6	2.0	0.0060	0.0098	PO***
PO880314	368.5	369.8	34	16.7	0.99	16.6	20.3	1.0	0.0085	0.0137	MFARD
PO880316	381.8	381.8	34	3.4	0.79	8.2	48.2	24.3	0.0076	0.0550	POAT
PO880317	381.4	381.4	34	6.0	0.89	8.2	34.9	15.6	0.0078	0.0266	POAT
PO880318	366.9	369.3	20	10.9	0.95	8.2	16.4	3.3	0.0035	0.0084	POAT
PO880322	370.0	370.0	34	3.3	0.81	16.6	39.2	19.9	0.0079	0.0591	MFARD
PO880323	355.5	355.5	34	6.2	0.88	16.6	22.7	1.3	0.0045	0.0186	MFARD
PO880325	369.9	369.9	34	3.3	0.85	8.2	33.3	26.0	0.0077	0.0609	POAT

* POAT: Average temperature increasing with a small hot-spot in the centerline temperature profile.

** MFARD: Non-pseudoadiabatic.

*** PO: All temperature profiles increasing.

Table 30: Operating Conditions, conversion, liquid production and liquid yield (PO reactor runs).

RUN #	PO 880201	PO 880203	PO 880204	PO 880208	PO 880210	PO 880212	PO 880225	PO 880302
Methane	3.1	1.8	1.7	2.5	3.4	2.8	3.5	3.3
Ethylene	1.4	1.3	0.0	0.5	0.5	0.3	1.4	1.2
Ethane	16.9	10.9	10.4	14.0	17.8	14.7	16.7	16.0
Propylene	0.0	0.5	0.0	0.05	0.13	0.1	0.12	0.1
Propane	14.1	8.7	11.2	12.7	15.0	13.6	13.7	13.4
i-Butane	7.7	1.7	2.0	1.5	1.8	3.0	6.5	5.8
n-Butane	0.0	2.2	1.6	2.5	2.5	2.2	3.1	3.0
Butenes	0.0	0.23	0.02	0.11	0.13	0.07	0.31	0.3
C_5^+ Hydrocarbons								
Paraffins + Cycloparaffins	3.9	8.0	2.3	4.2	4.3	4.0	10.4	9.4
Olefins + Cycloolefins	0.0	3.3	0.02	0.0	0.0	0.1	0.2	0.2
Aromatics	47.6	52.4	58.1	48.3	40.8	48.1	40.7	42.9
C_{11}^+	5.2	8.9	12.7	13.7	13.5	10.9	3.4	4.2
C_5^+ Hydrocarbons Product Distribution								
C_5 - C_8 Saturates	6.8	10.9	3.1	6.3	6.9	6.4	18.9	16.5
C_5 - C_8 Unsaturates	0.04	4.5	0.03	0.0	0.0	0.2	0.4	0.3
C_9^+ P+O+N	0.02	0.01	0.0	0.0	0.4	0.01	0.02	0.05
Benzene	0.12	0.2	0.18	0.23	0.5	0.2	0.4	0.4
Toluene	2.1	2.7	1.6	1.4	2.1	1.4	2.9	2.6
C_8 Aromatics	23.1	15.5	13.3	11.1	1.2	11.6	21.5	21.7
C_9 Aromatics	41.8	35.5	36.2	32.3	24.0	34.0	36.1	38.5
C_{10} Aromatics	16.8	18.2	28.1	27.9	41.6	28.7	13.4	12.2
C_{11} Aromatics	5.2	6.0	8.1	8.7	16.3	7.9	3.2	3.8
C_{12} Aromatics	2.5	3.3	5.0	6.5	3.0	4.6	1.5	1.8
C_{13} Aromatics	0.93	1.7	2.6	3.3	1.9	2.5	1.5	0.9
C_{14} Aromatics	0.39	0.51	1.0	0.6	1.6	0.8	0.1	0.4
C_{15} Aromatics	0.15	0.62	0.8	1.7	0.3	1.6	0.0	0.6

Table 31a: Hydrocarbons Distribution

RUN #	PO 880304	PO 880307	PO 880308	PO 880309	PO 880314	PO 880316	PO 880317	PO 880318
Methane	2.6	2.8	2.6	2.1	3.3	3.7	4.5	3.6
Ethylene	1.8	2.0	0.3	3.2	2.6	0.3	0.7	2.7
Ethane	15.3	13.9	13.8	12.8	15.9	16.6	20.3	14.9
Propylene	0.7	0.2	0.13	0.9	0.08	0.2	0.4	0.0
Propane	12.2	10.5	12.0	8.4	11.1	14.8	16.8	11.1
i-Butane	2.4	4.6	2.7	3.5	6.0	1.5	6.0	8.4
n-Butane	3.0	2.4	2.0	2.0	2.7	2.5	3.4	2.2
Butenes	4.9	0.3	1.5	0.2	0.4	0.07	0.2	0.5
C_5^+ Hydrocarbons								
Paraffins + Cycloparaffins	7.3	7.8	6.0	8.9	12.5	4.5	6.6	13.3
Olefins + Cycloolefins	4.6	0.8	2.6	0.9	1.1	1.2	2.2	0.07
Aromatics	41.9	48.5	48.5	51.3	40.0	47.5	33.4	34.1
C_{11}^+	3.2	6.3	7.8	5.7	4.3	7.0	5.3	9.0
C_5^+ Hydrocarbons Product Distribution								
C_5 - C_8 Saturates	12.7	12.2	9.2	13.2	21.5	7.5	13.8	23.5
C_5 - C_8 Unsaturates	8.1	1.2	4.0	1.4	1.9	2.0	4.6	0.12
C_9^+ P+O+N	0.07	0.07	0.0	0.08	0.07	0.0	0.0	0.0
Benzene	0.09	0.12	2.3	0.05	0.07	0.2	0.4	0.8
Toluene	2.5	2.6	1.3	2.0	1.3	0.3	0.6	1.8
C_8 Aromatics	19.5	19.8	12.0	15.0	17.0	14.3	13.4	11.8
C_9 Aromatics	37.6	36.2	32.6	36.1	33.7	37.3	34.2	26.5
C_{10} Aromatics	13.7	17.8	26.4	23.6	17.0	26.7	21.4	19.3
C_{11} Aromatics	3.3	4.7	6.4	4.7	4.2	6.5	5.8	6.3
C_{12} Aromatics	1.3	1.7	2.7	1.8	1.6	2.7	2.4	4.4
C_{13} Aromatics	0.6	3.0	1.6	1.2	0.6	1.4	1.6	3.6
C_{14} Aromatics	0.2	0.2	0.6	0.4	0.2	0.4	0.6	0.8
C_{15} Aromatics	0.2	0.2	0.9	0.4	0.8	0.5	0.9	0.7

Table 31b: Hydrocarbons Distribution

RUN #	PO 880322	PO 880323	PO 880325
Methane	2.3	2.5	2.6
Ethylene	0.4	1.5	0.4
Ethane	12.2	15.8	13.2
Propylene	0.2	0.5	0.2
Propane	9.7	10.6	10.0
i-Butane	2.7	3.5	3.0
n-Butane	1.8	2.2	1.9
Butenes	0.1	0.07	0.0
C_5^+ Hydrocarbons			
Paraffins + Cycloparaffins	3.9	7.5	4.5
Olefins + Cycloolefins	0.1	0.0	0.0
Aromatics	55.9	46.2	55.3
C_{11}^+	10.7	9.7	8.9
C_5^+ Hydrocarbons Product Distribution			
C_5 - C_8 Saturates	5.5	11.8	6.5
C_5 - C_8 Unsaturates	0.12	0.0	0.0
C_9^+ P+O+N	0.0	0.0	0.0
Benzene	0.1	0.2	0.2
Toluene	1.4	1.1	1.2
C_8 Aromatics	11.6	10.0	11.8
C_9 Aromatics	34.3	31.9	35.1
C_{10} Aromatics	31.6	29.6	32.2
C_{11} Aromatics	7.5	8.2	7.1
C_{12} Aromatics	3.2	3.2	2.6
C_{13} Aromatics	2.6	2.0	1.5
C_{14} Aromatics	0.7	0.8	0.6
C_{15} Aromatics	1.1	1.0	1.2

Table 31c: Hydrocarbons Distribution

conversions and higher liquid productivities, are achieved in the Pseudoadiabatic unit with longer residence times. A similar explanation can be advanced to justify the fraction of C_{5+} hydrocarbons obtained in the Pseudoadiabatic Reactor (up to 73.1%) which was sometimes higher than the maximum observed in the Berty well-agitated reactor (around 60%). It has to be pointed out that for the same synthesis gas composition and similar residence times, the Berty reactor operates with higher partial pressures of hydrogen than the Pseudoadiabatic Reactor. Consequently hydrogenation of olefins are enhanced in the Berty reactor with respect to the Pseudoadiabatic unit. The Pseudoadiabatic reactor revealed then, according to these results, as an excellent tool to control the hydrogenation side reaction and to achive high selectivities.

b. Temperature profile

The experimental results, in terms of temperature profiles, are gathered in appendix J for all the runs. An example of the report for runs PO880203 is given in Table 32. This table, describing the temperature profile, was generated by the computer program PROFIL presented in appendix M.

Table 32 contains the temperature readings just before the feeding of the reactant, the temperature readings during the reaction and the revised temperature profile. The revised temperature profile was obtained from the temperature readings during the runs and the initial readings. The revision of the temperature profiles was necessary to account for the slightly uneven temperature reading distribution prior to start-up. The method employed for the standardization is as follows:

1) From the initial readings, the temperature deviation with respect to a thermocouple located at the 0.006 m height was calculated for the three radial

Table 32: Example of temperature profile printout

```
                  *****************************************
                  *                                       *
                  *          TEMPERATURE PROFILE          *
                  *             RUN P0880203              *
                  *                                       *
                  *****************************************


                TEMPERATURE READINGS BEFORE REACTANTS FEEDING
                ---------------------------------------------

                           ** REACTOR SIDE **

                  x (m)        TC (C)       TH (C)       TW (C)

     LEVEL   1    0.006        367.7        367.0        367.1
     LEVEL   2    0.156        367.9        367.6        366.7
     LEVEL   3    0.356        367.6        366.3        366.5
     LEVEL   4    0.556        365.0        365.3        364.8
     LEVEL   5    0.756        366.2        366.1        364.0
     LEVEL   6    0.956        367.3        367.2        365.6
     LEVEL   7    1.156        368.7        367.9        365.7
     LEVEL   8    1.356        367.7        365.6        365.5
     LEVEL   9    1.556        365.1        364.2        363.1
     LEVEL  10    1.706        366.7        365.2        365.5

                           ** COOLANT SIDE **

                  x (m)        TC (C)

     LEVEL   1    0.056        367.2
     LEVEL   2    0.456        360.1
     LEVEL   3    0.856        361.9
     LEVEL   4    1.256        365.6
     LEVEL   5    1.656        365.4

     INITIAL MEAN TEMPERATURE: 366.23
     INITIAL COOLANT TEMPERATURE: 364.04

                  TEMPERATURE READINGS DURING THE REACTION
                  ----------------------------------------

                           ** REACTOR SIDE **

                  x (m)        TC (C)       TH (C)       TW (C)       TAV (C)

     LEVEL   1    0.006        383.5        372.4        371.1        374.8
     LEVEL   2    0.156        383.3        377.8        372.3        377.0
     LEVEL   3    0.356        382.3        376.6        374.3        377.2
     LEVEL   4    0.556        377.2        375.2        374.3        375.4
     LEVEL   5    0.756        377.8        376.3        374.3        375.9
     LEVEL   6    0.956        379.3        377.9        376.1        377.5
     LEVEL   7    1.156        380.8        379.3        377.1        378.8
     LEVEL   8    1.356        379.9        377.2        376.1        377.5
     LEVEL   9    1.556        377.1        375.9        374.6        375.7
     LEVEL  10    1.706        379.9        377.1        377.2        377.9
```

```
                    ** COOLANT SIDE **

                 x (m)        TC (C)

LEVEL    1       0.056        372.2
LEVEL    2       0.456        365.7
LEVEL    3       0.856        373.6
LEVEL    4       1.256        375.4
LEVEL    5       1.656        374.6


         REVISED TEMPERATURE PROFILE FOR THE REACTION
         --------------------------------------------

                   ** REACTOR SIDE **

                 x (m)        TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1       0.006        383.5        372.4        371.1        374.8
LEVEL    2       0.156        383.1        377.2        372.7        376.9
LEVEL    3       0.356        382.4        377.3        374.9        377.7
LEVEL    4       0.556        379.9        376.9        376.6        377.6
LEVEL    5       0.756        379.3        377.2        377.4        377.9
LEVEL    6       0.956        379.7        377.7        377.6        378.2
LEVEL    7       1.156        379.8        378.4        378.5        378.8
LEVEL    8       1.356        379.9        378.6        377.7        378.6
LEVEL    9       1.556        379.7        378.7        378.6        378.9
LEVEL    10      1.706        380.9        378.9        378.8        379.4

                   ** COOLANT SIDE **

                 x (m)        TC (C)

LEVEL    1       0.056        372.2
LEVEL    2       0.456        372.8
LEVEL    3       0.856        378.9
LEVEL    4       1.256        377.0
LEVEL    5       1.656        376.4
```

positions (gas side) and for one axial position (coolant side).

2) These temperature deviations were used to correct the temperature readings and to generate the revised temperature profiles.

Furthermore, it has to be pointed out that the x variable that appears in Table 32 between the level number and the temperature profile is the actual bed length.

Another important parameter to assess for each experimental run was T_{av}. The T_{av} value is the average temperature in the cross sectional area, and represents a weighed average of the temperatures at three reactor radial positions. The average was calculated with the following relationship:

$$T_{av} = 7/26\ T_{r=0} + 8/26\ T_{r=R/2} + 11/26\ T_{r=R}$$

The weighted average is derived from the integration of a parabolic profile on a circular surface as described by Froment and Bischoff (1979).

The revised temperature profiles are plotted in Figures 18-1 to 18-19. Temperature profiles are either fully Pseudoadiabatic (all temperature profiles increasing) (Run P0880314), Pseudoadiabatic for the Average Temperature (average temperature increasing with a small hot-spot in the centerline temperature profile) (Runs P0880201-P0880204, P0880210-P0880309, P0880317-P0880318, P0880325) or non-Pseudoadiabatic (all temperature profiles increasing with a small hot-spot) (Runs P0880208, P0880316, P0880322, P0880323).

Figure 18-1 to 18-19

Revised Temperature Profile

gas	○	centre
	●	middle
	Δ	wall
coolant	▲	
____		average temperature
......		simulated temperature

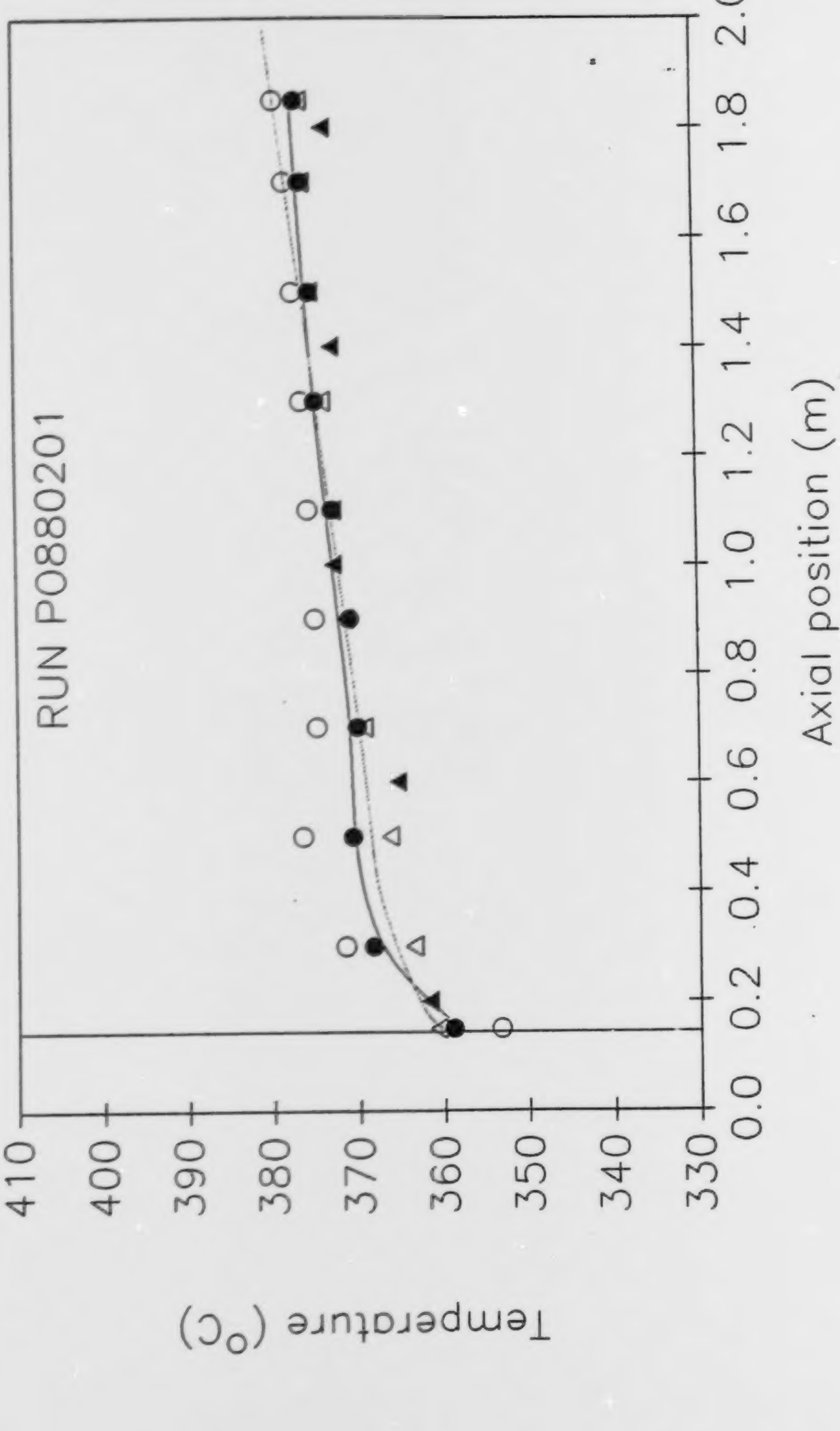


Figure 18-1: Revised temperature profile.

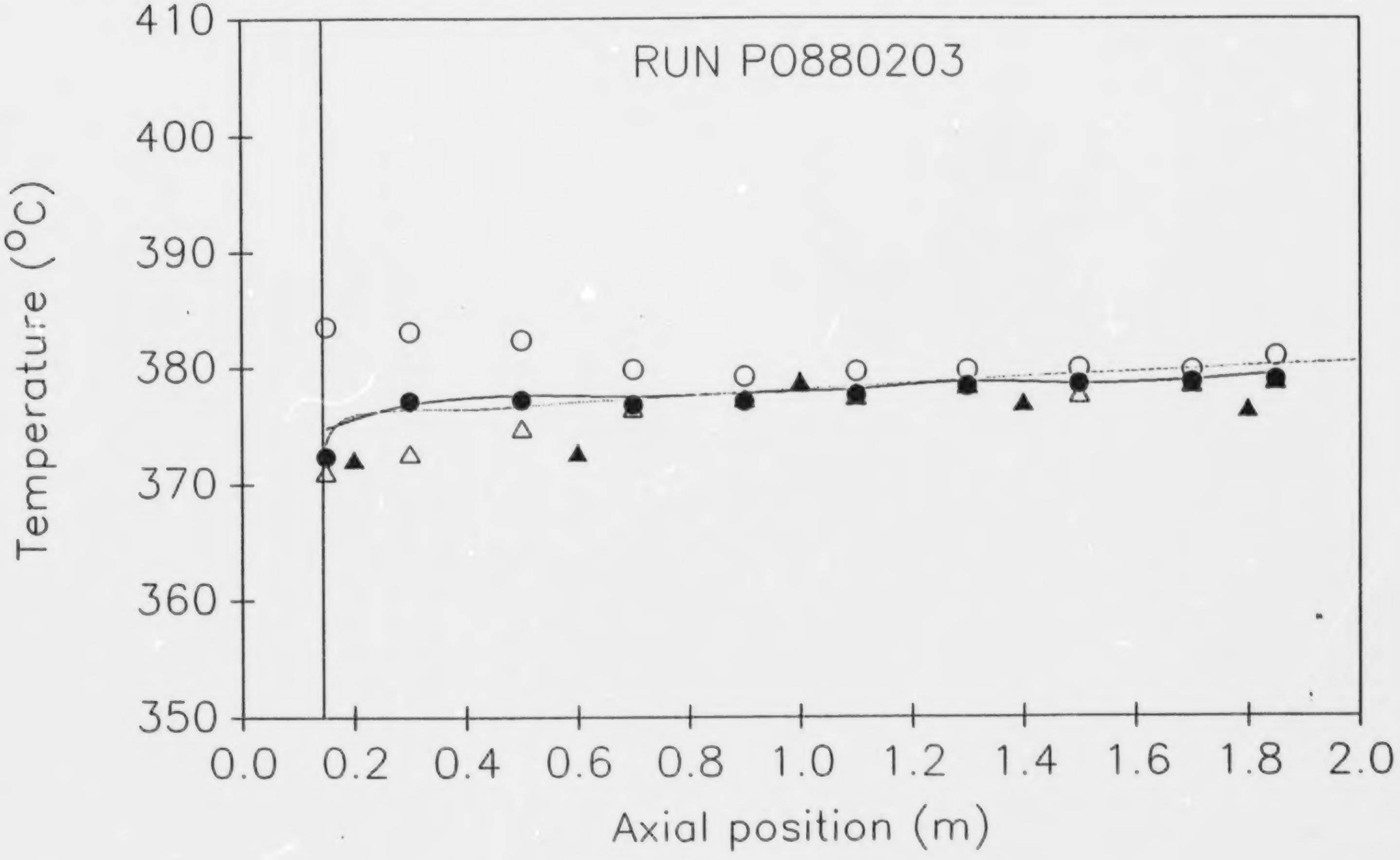


Figure 18-2: Revised temperature profile.

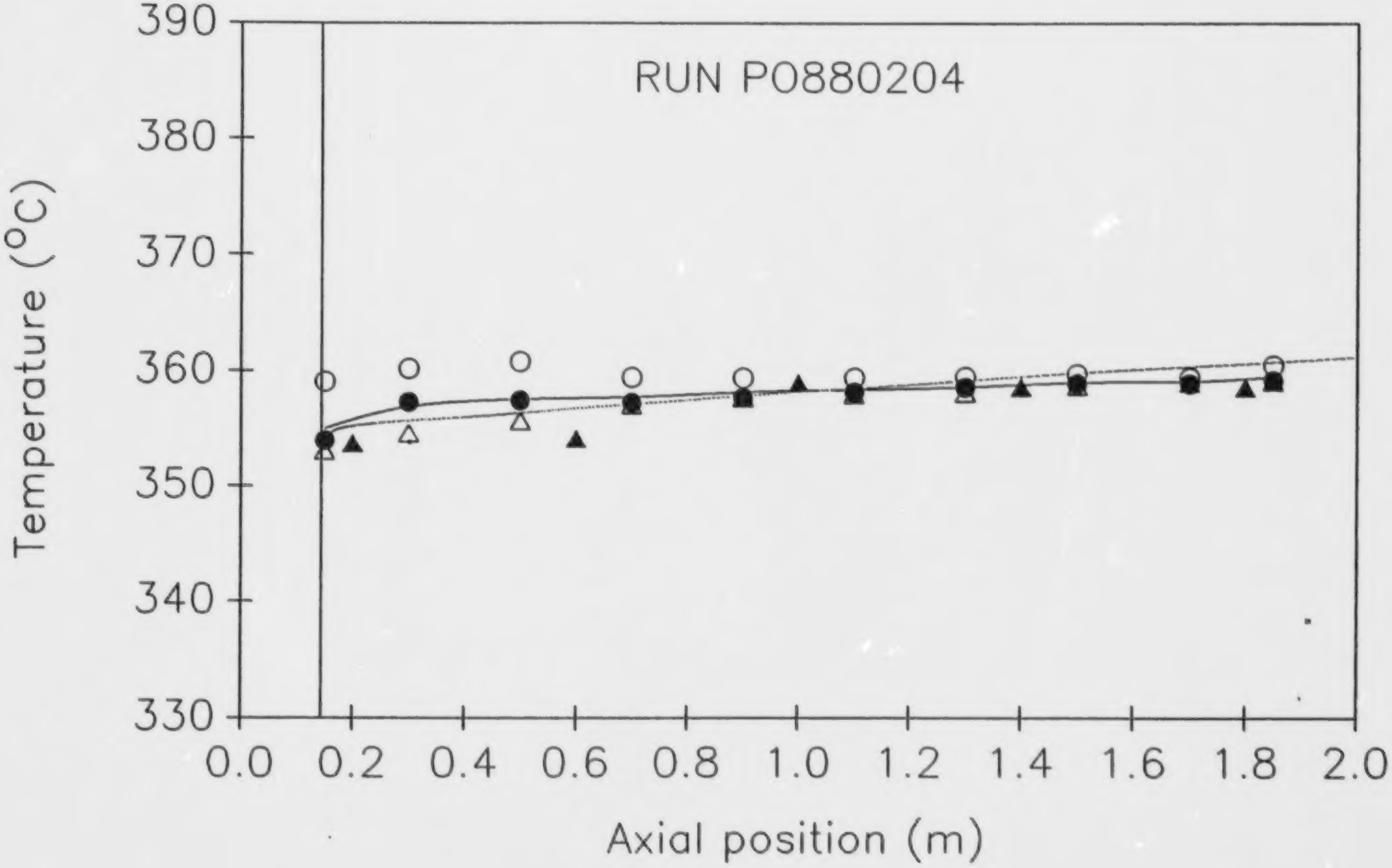


Figure 18-3: Revised temperature profile.

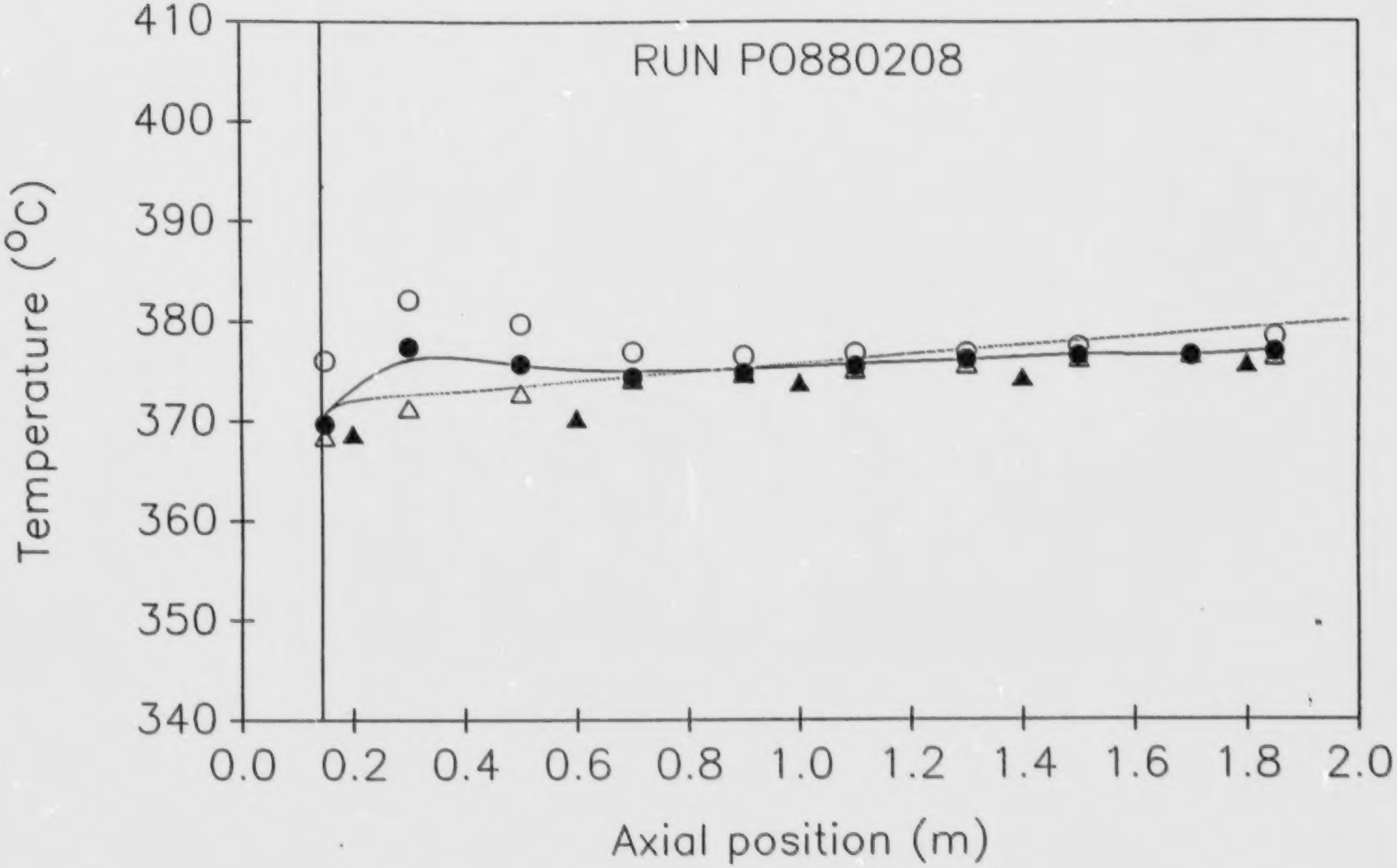


Figure 18-4: Revised temperature profile.

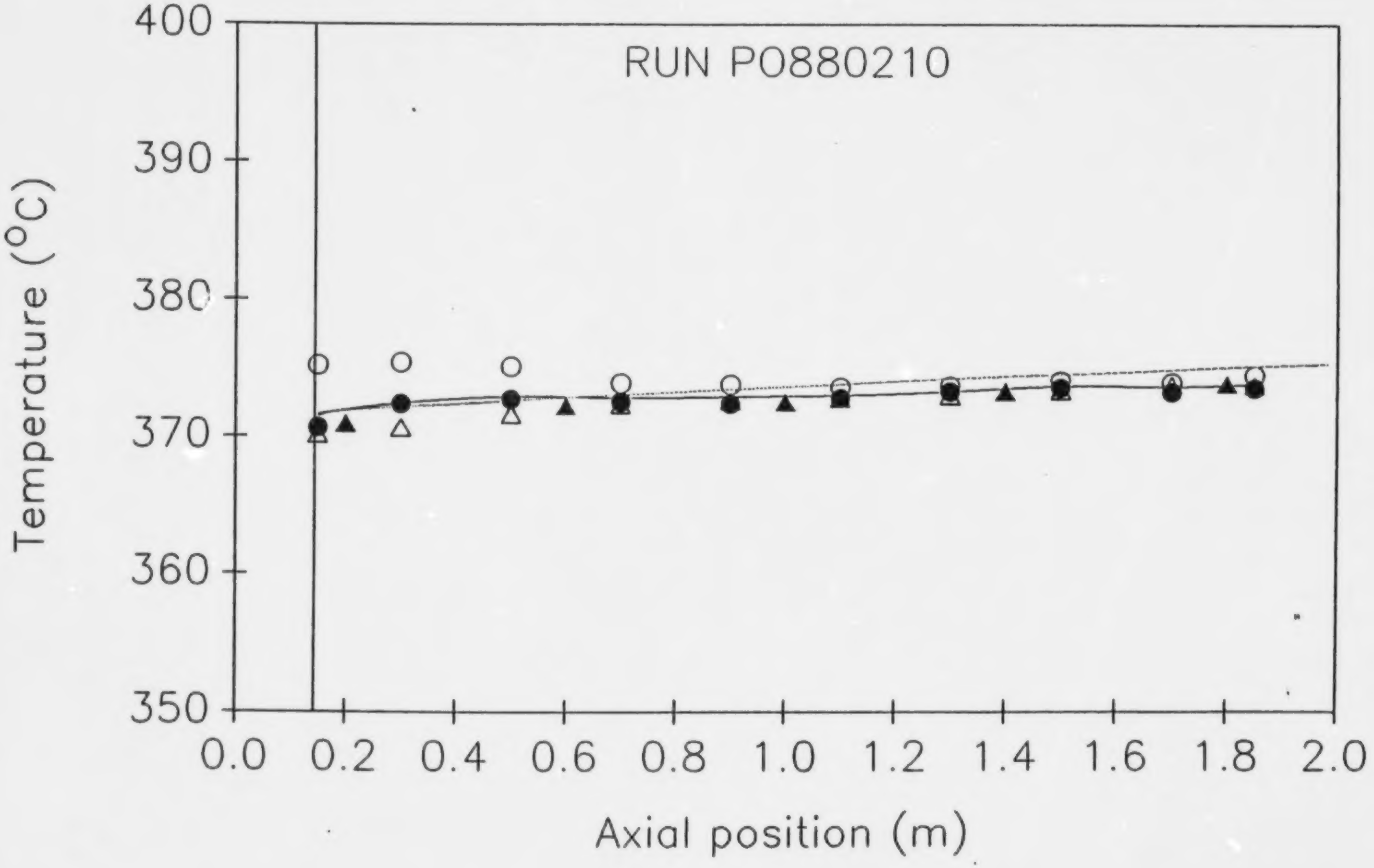


Figure 18-5: Revised temperature profile.

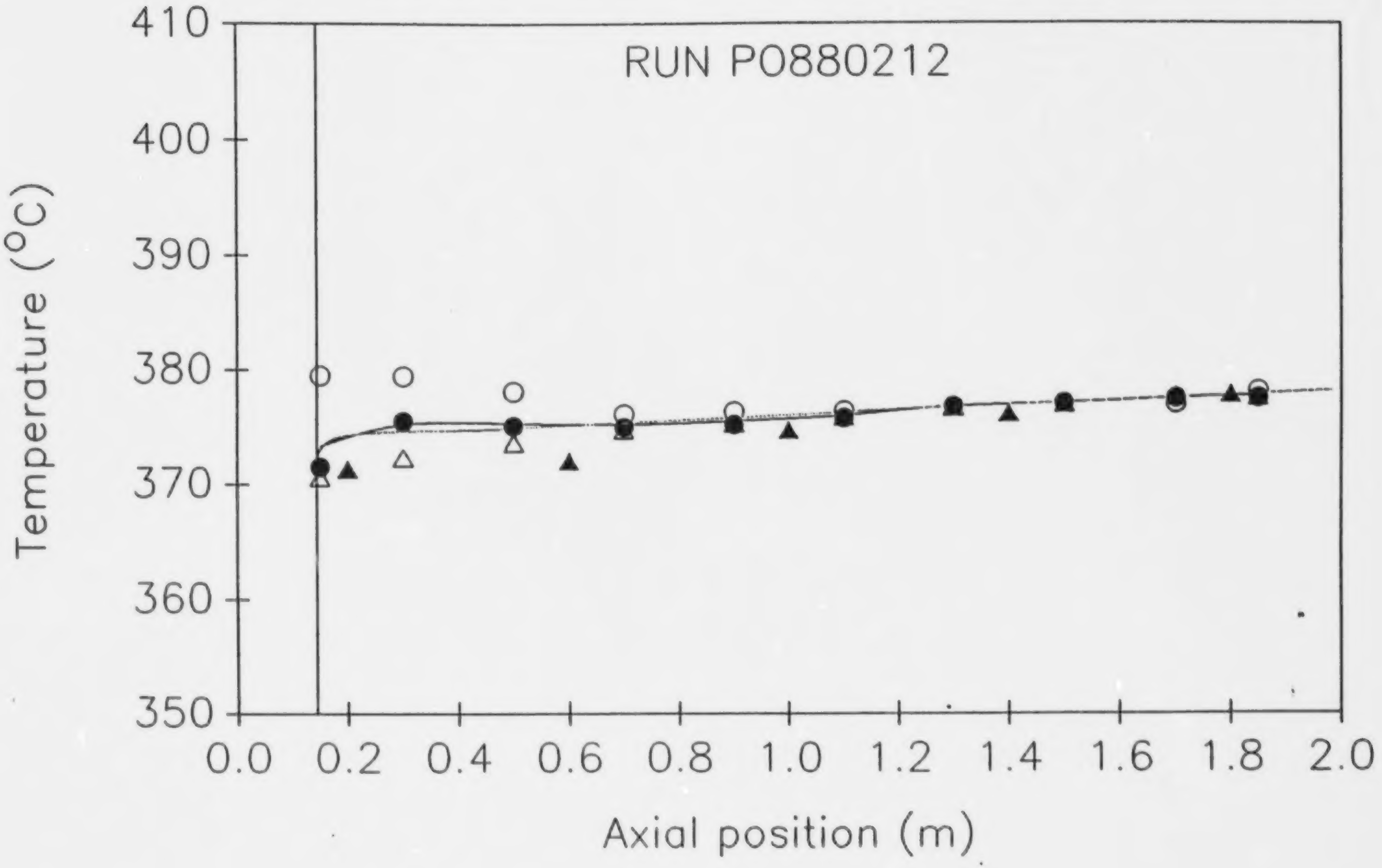


Figure 18-6: Revised temperature profile.

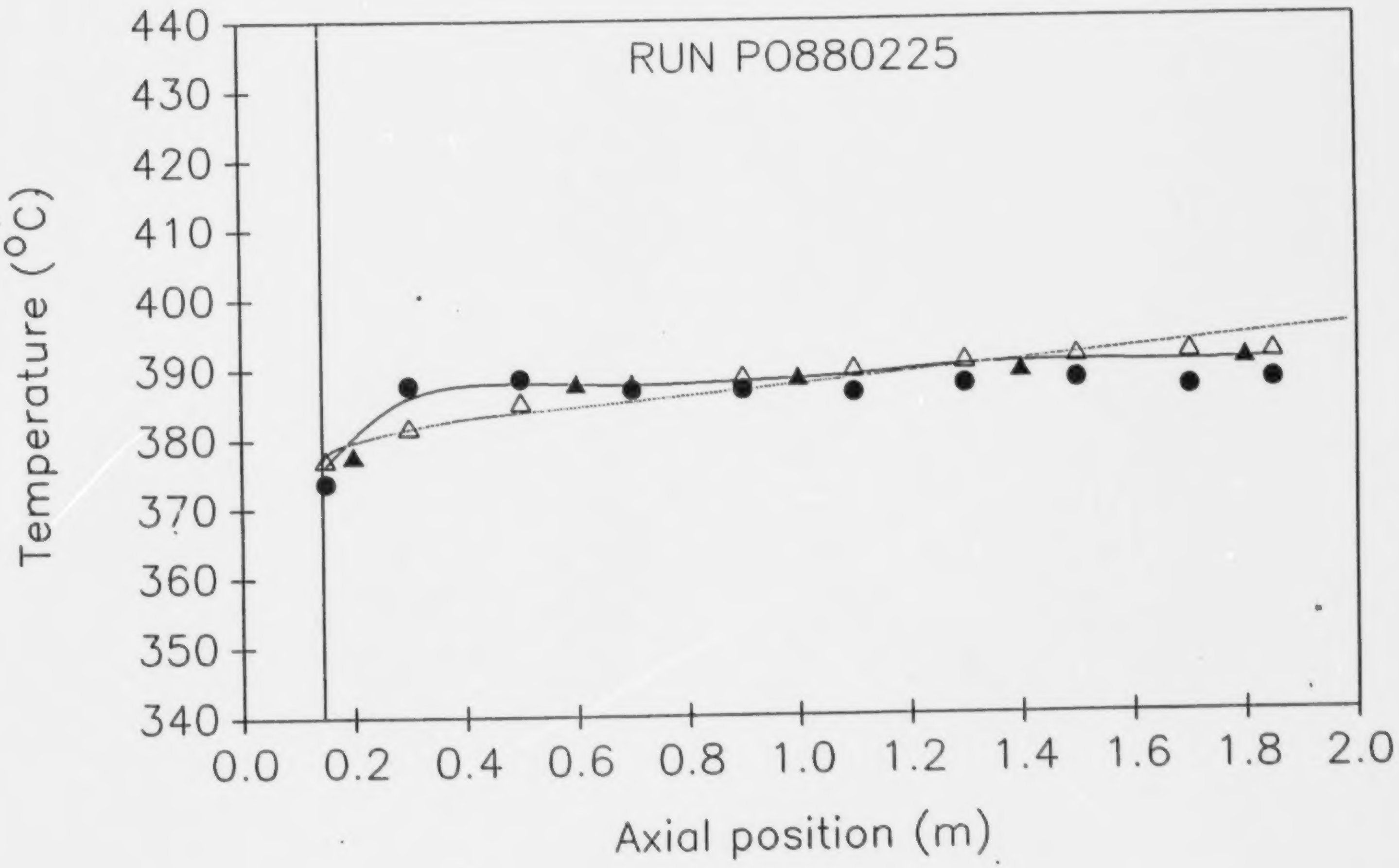


Figure 18-7: Revised temperature profile.

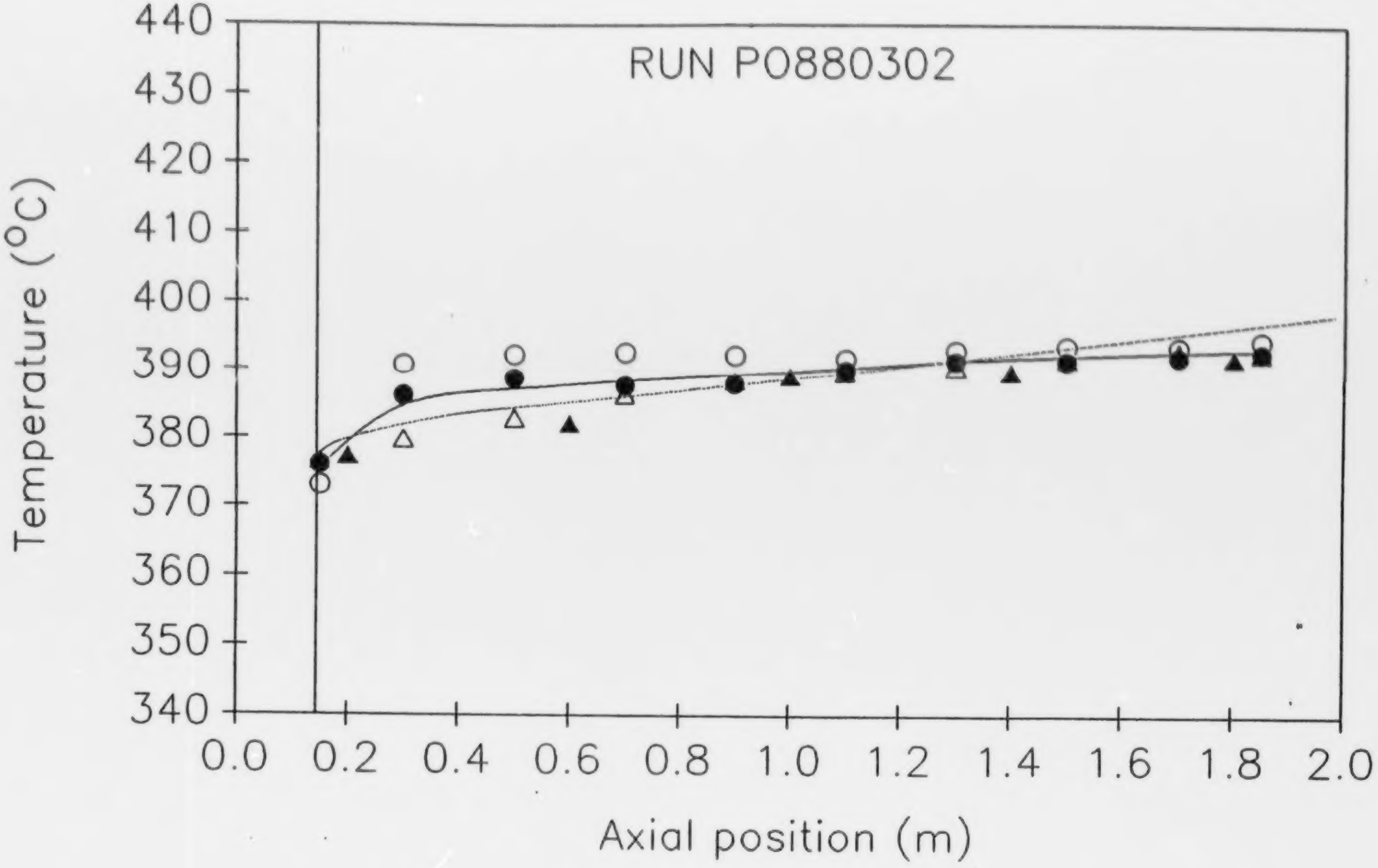


Figure 18-8: Revised temperature profile.

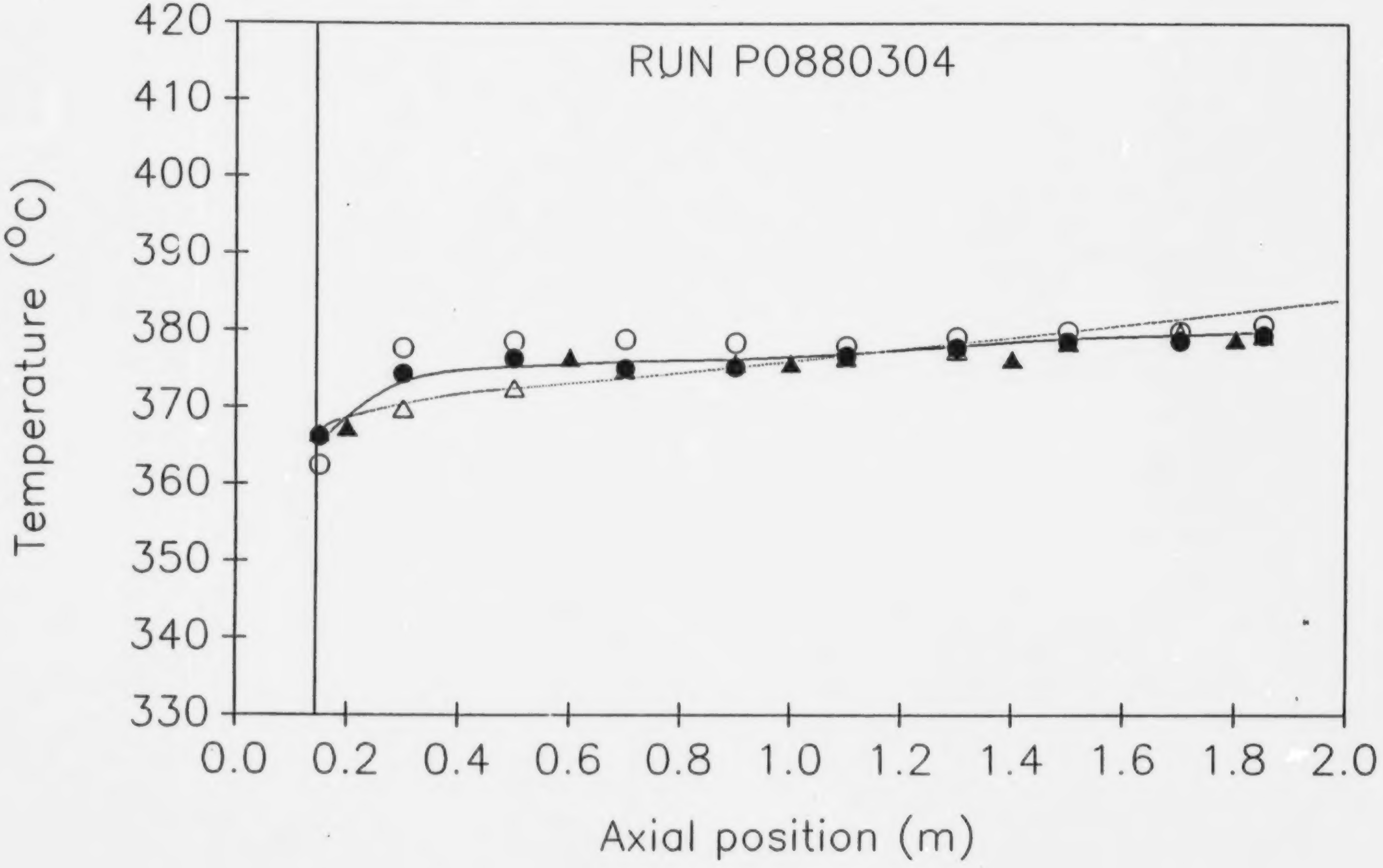


Figure 18-9: Revised temperature profile.

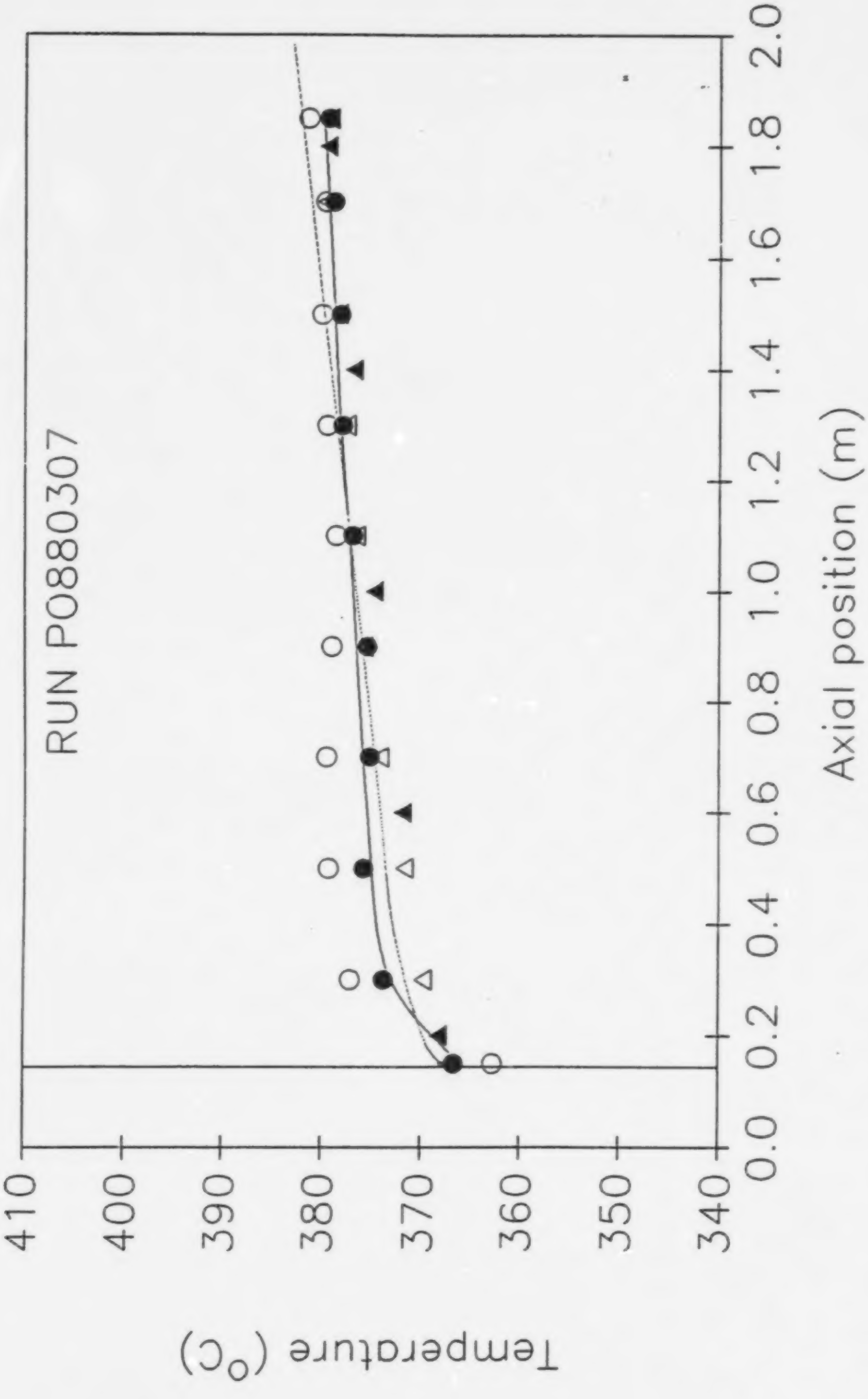


Figure 18-10: Revised temperature profile.

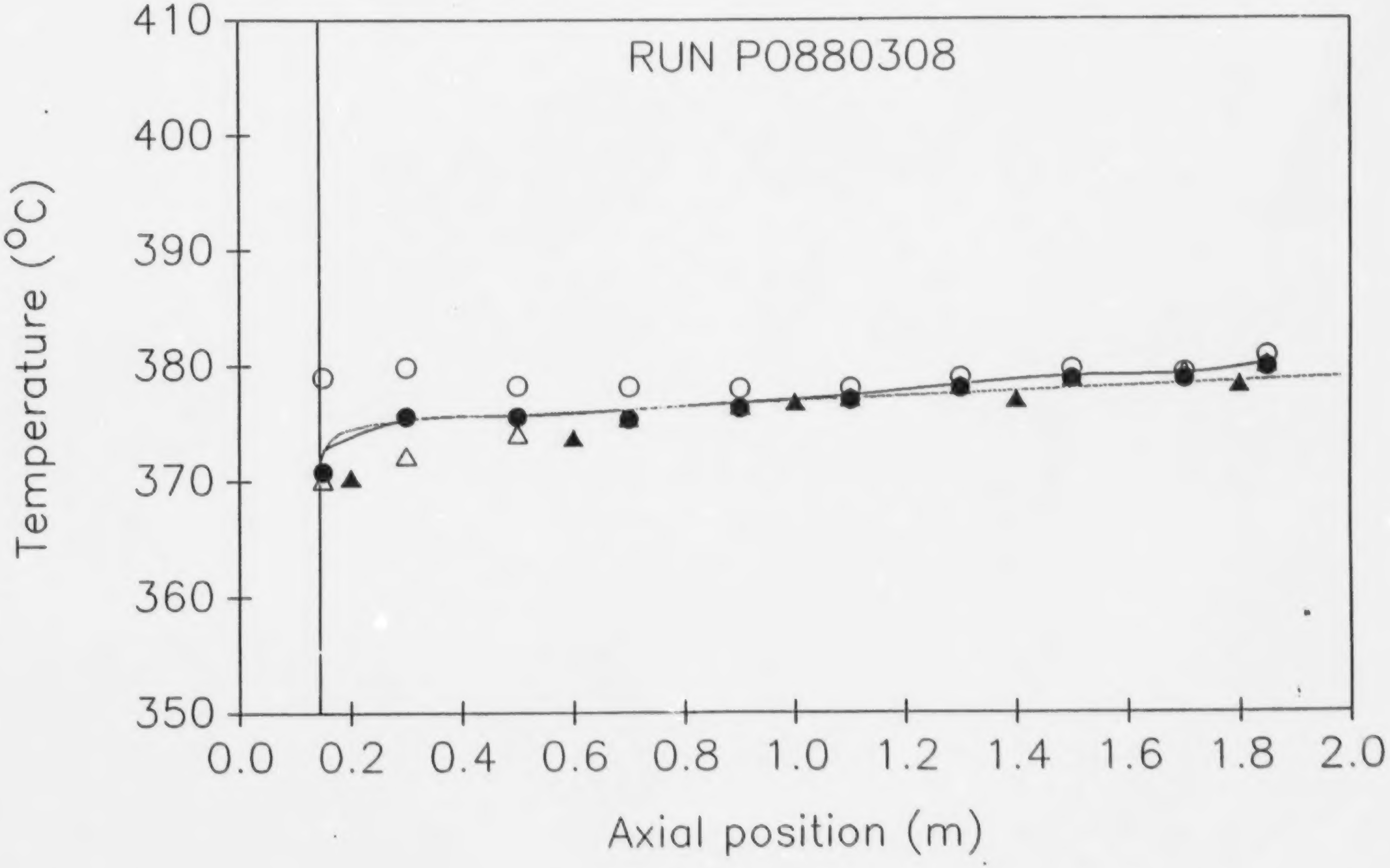


Figure 18-11: Revised temperature profile.

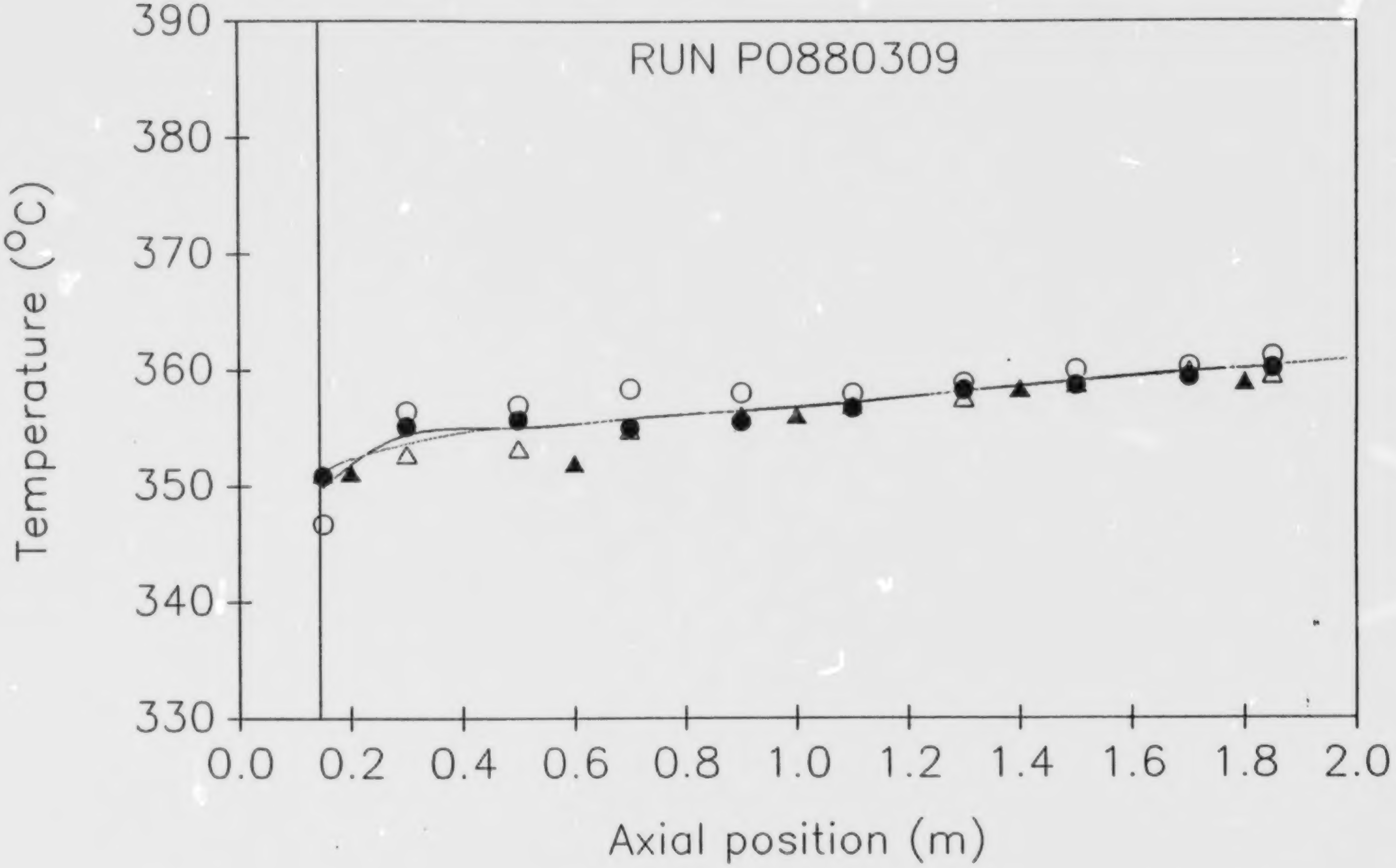


Figure 18-12: Revised temperature profile.

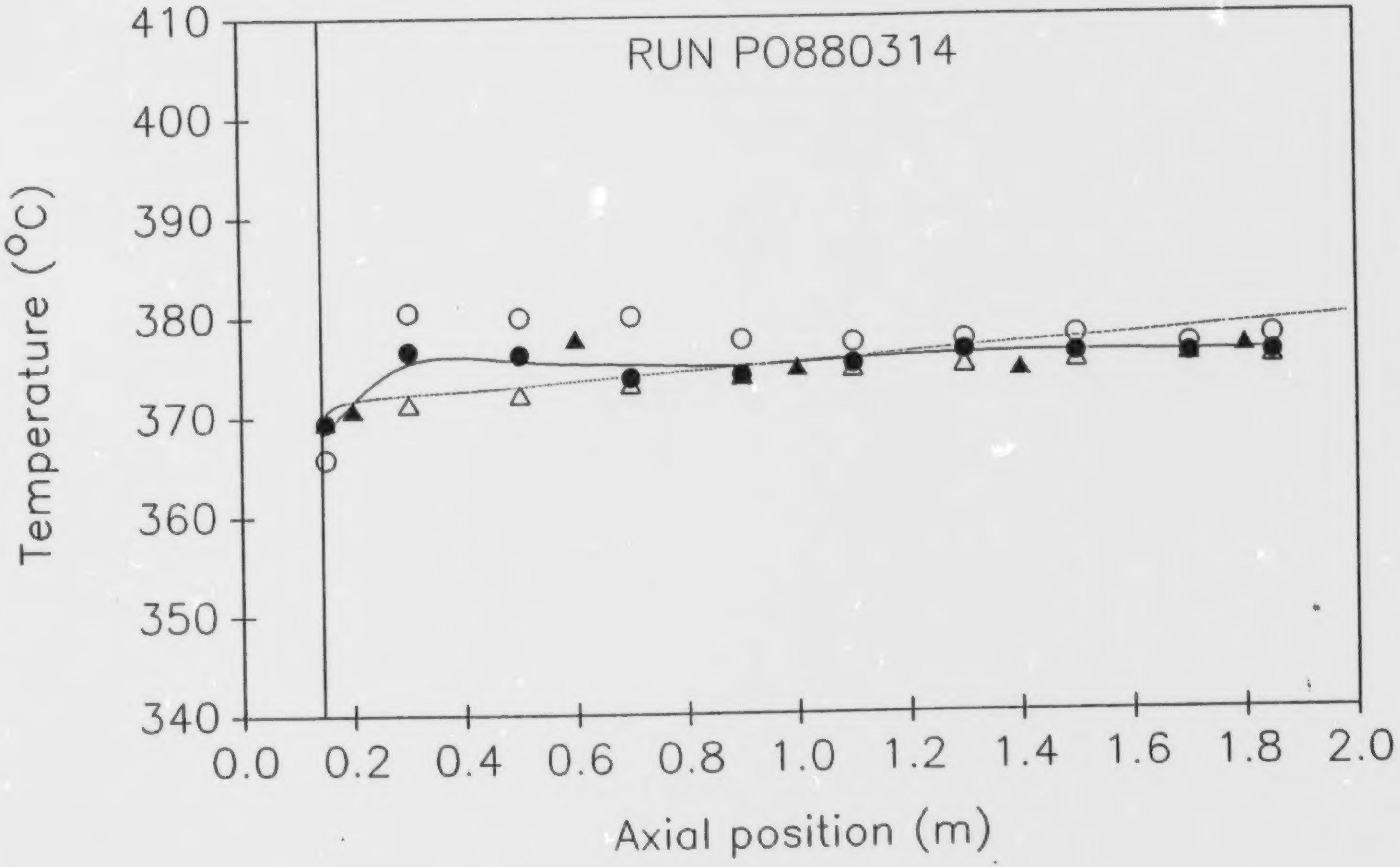


Figure 18-13: Revised temperature profile.

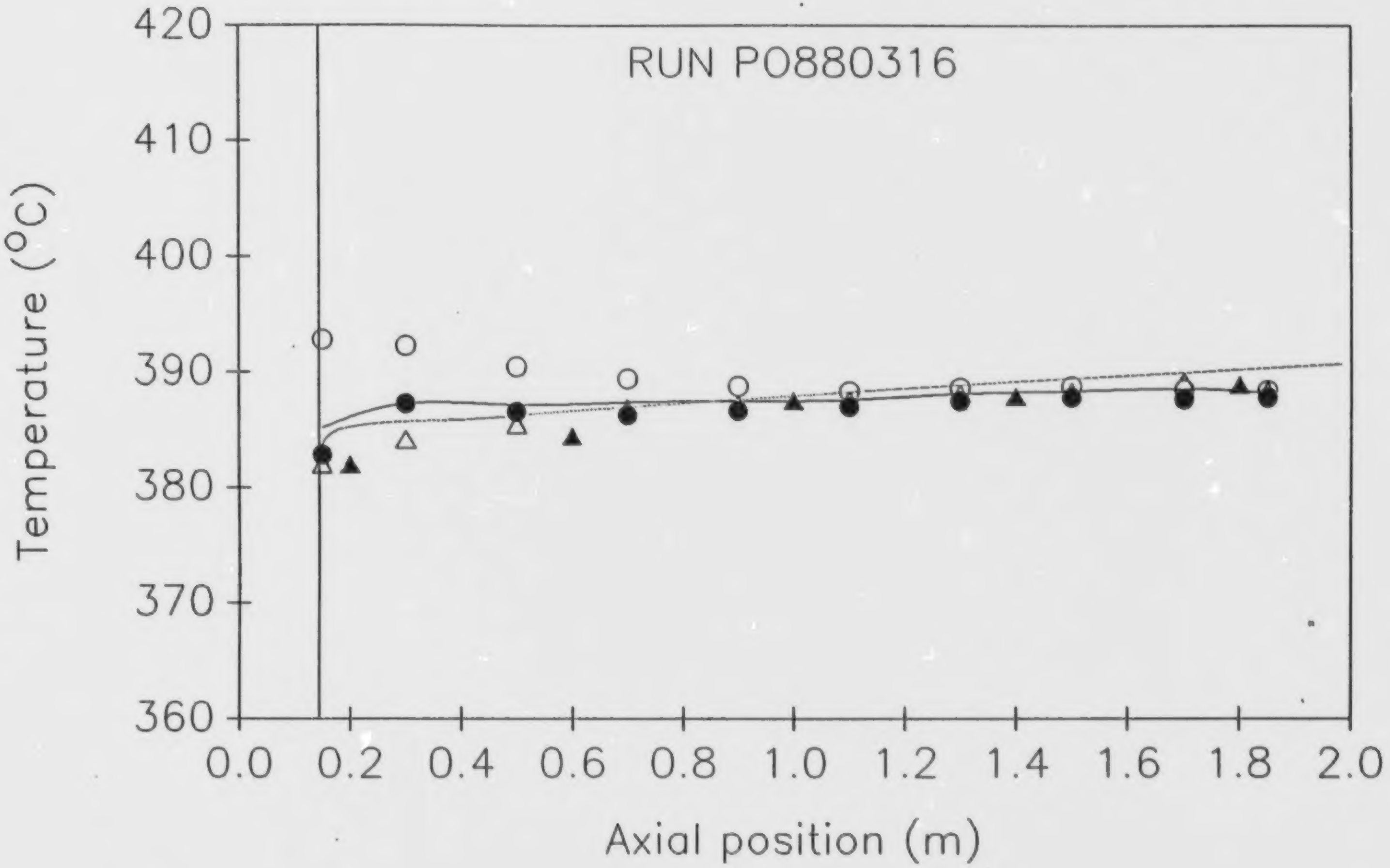


Figure 18-14: Revised temperature profile.

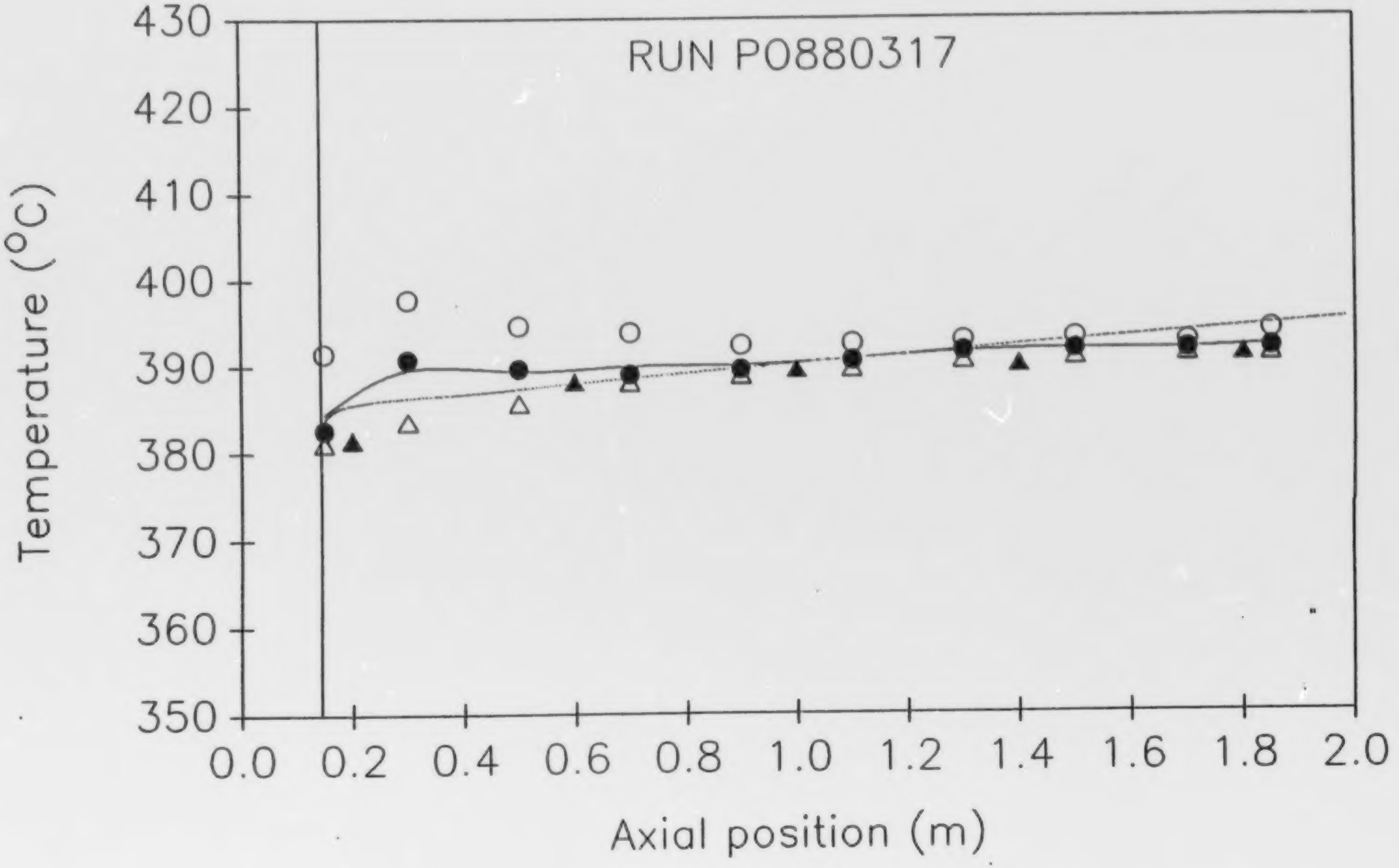


Figure 18-15: Revised temperature profile.

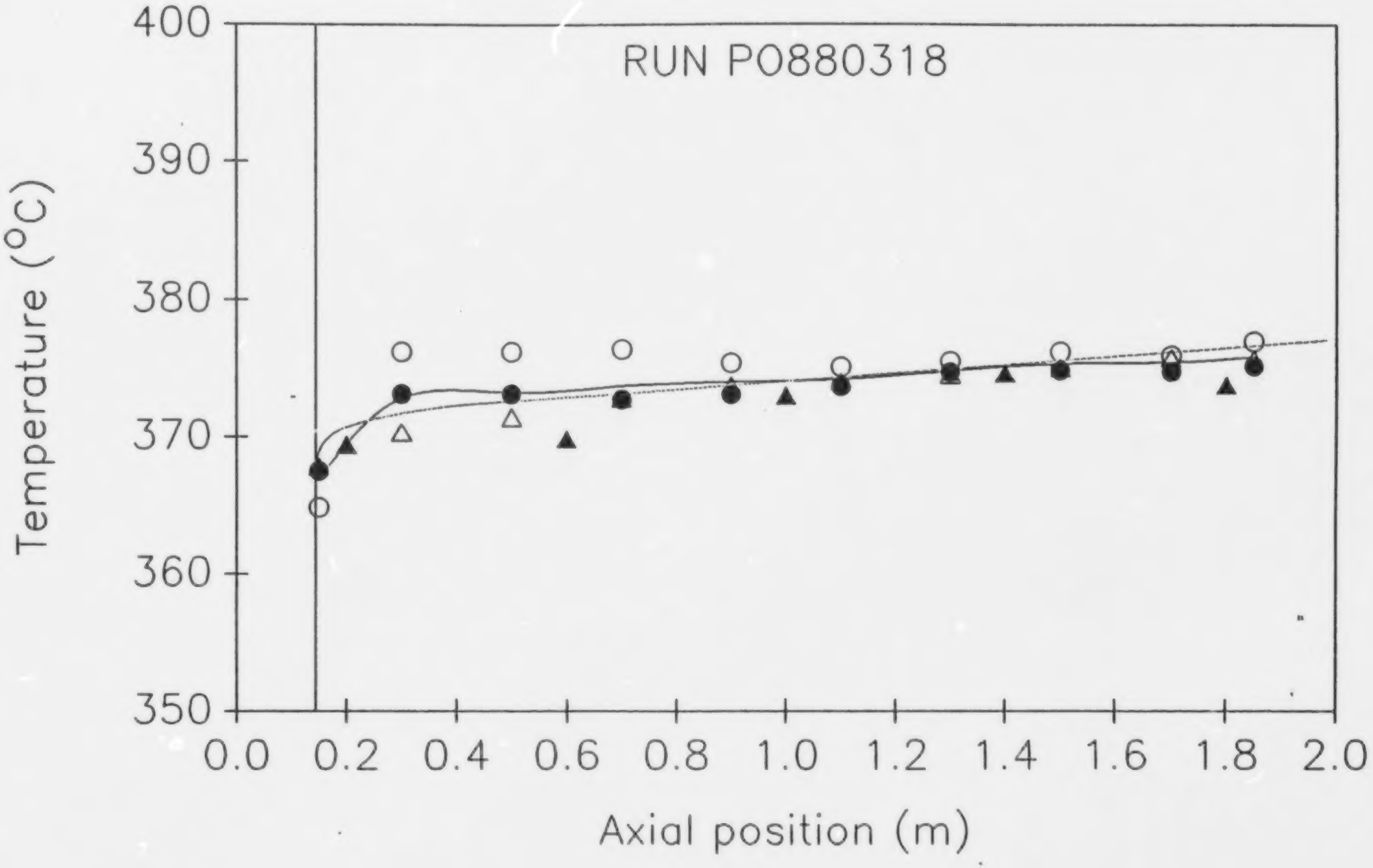


Figure 18-16: Revised temperature profile.

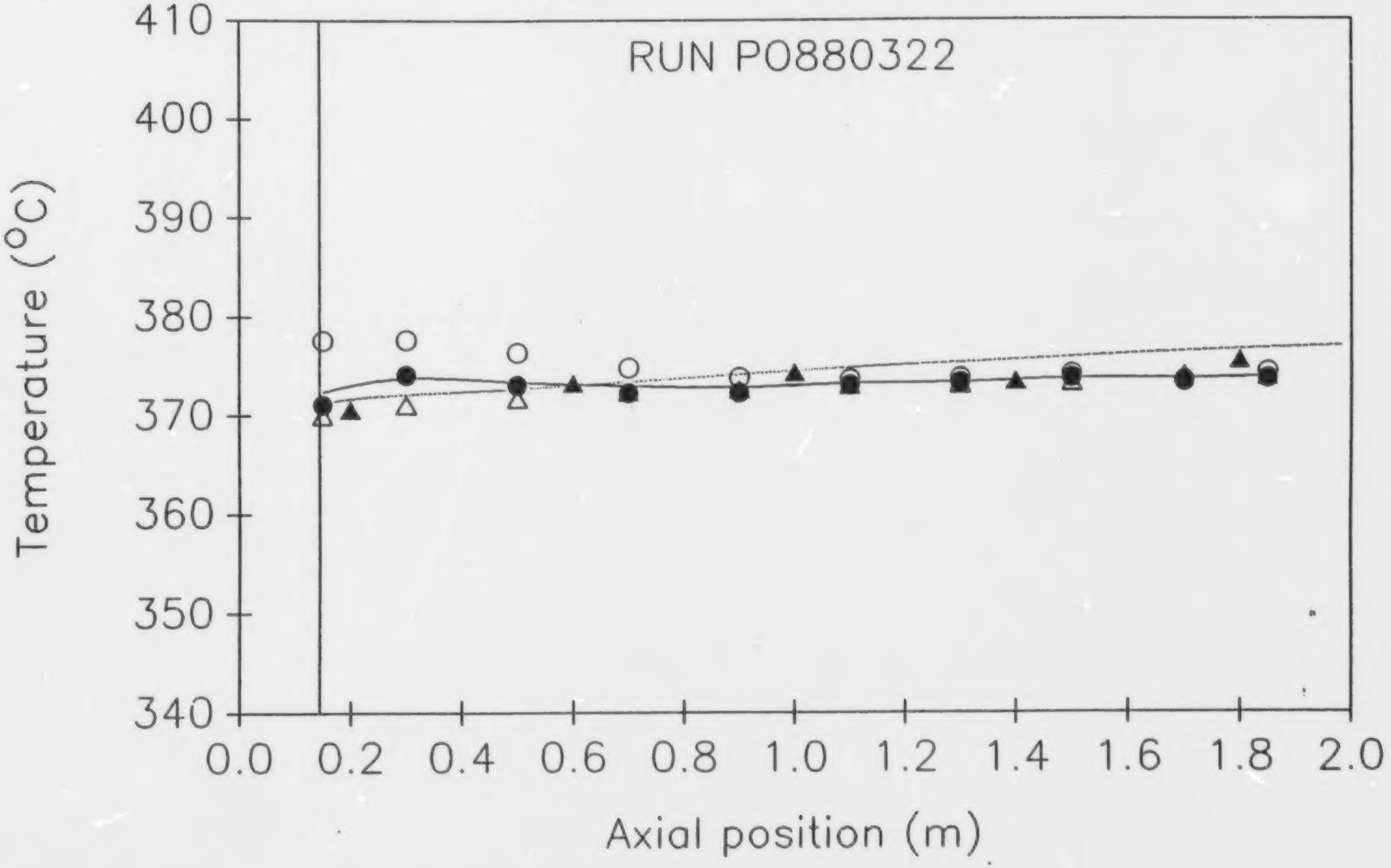


Figure 18-17: Revised temperature profile.

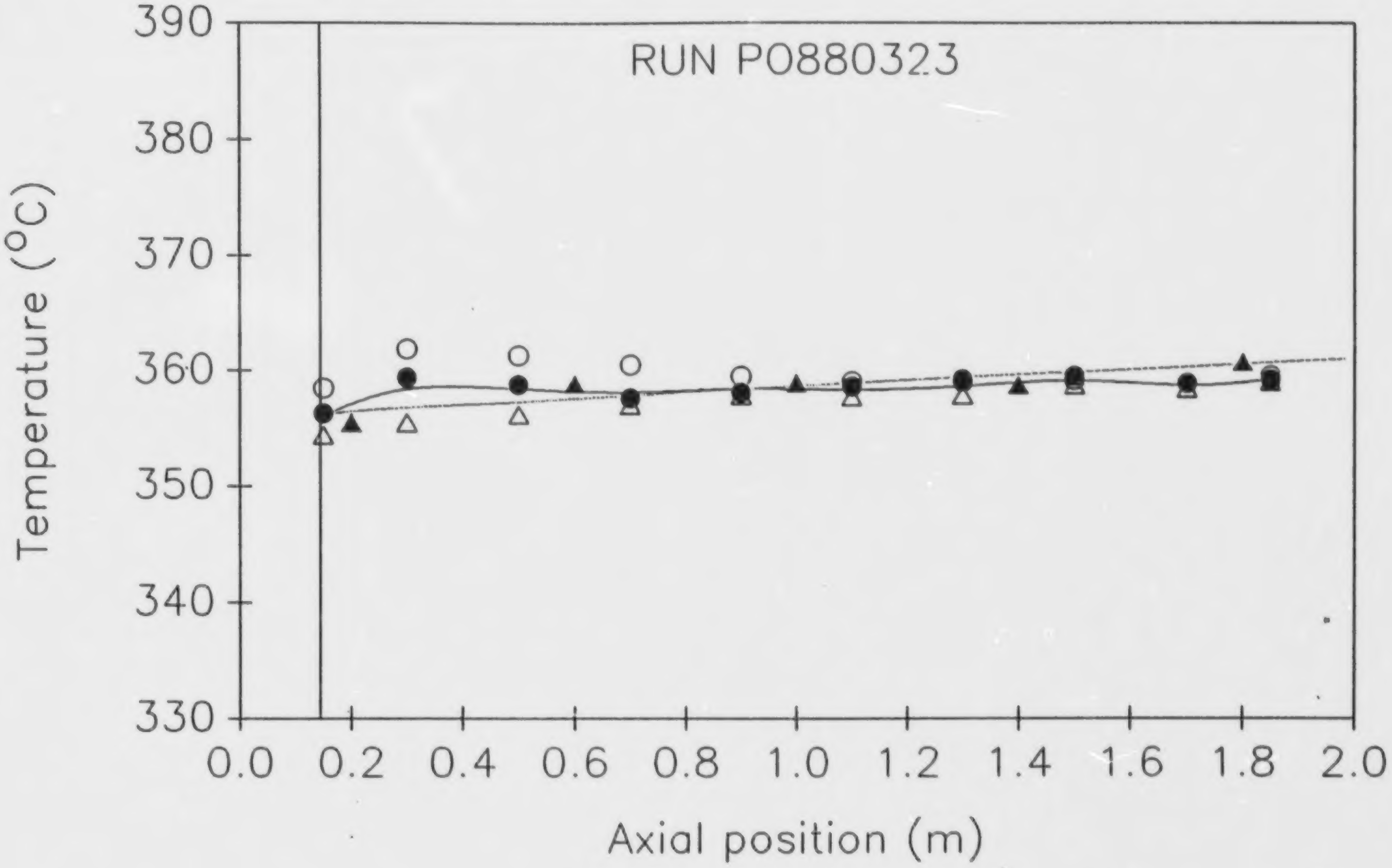


Figure 18-18: Revised temperature profile.

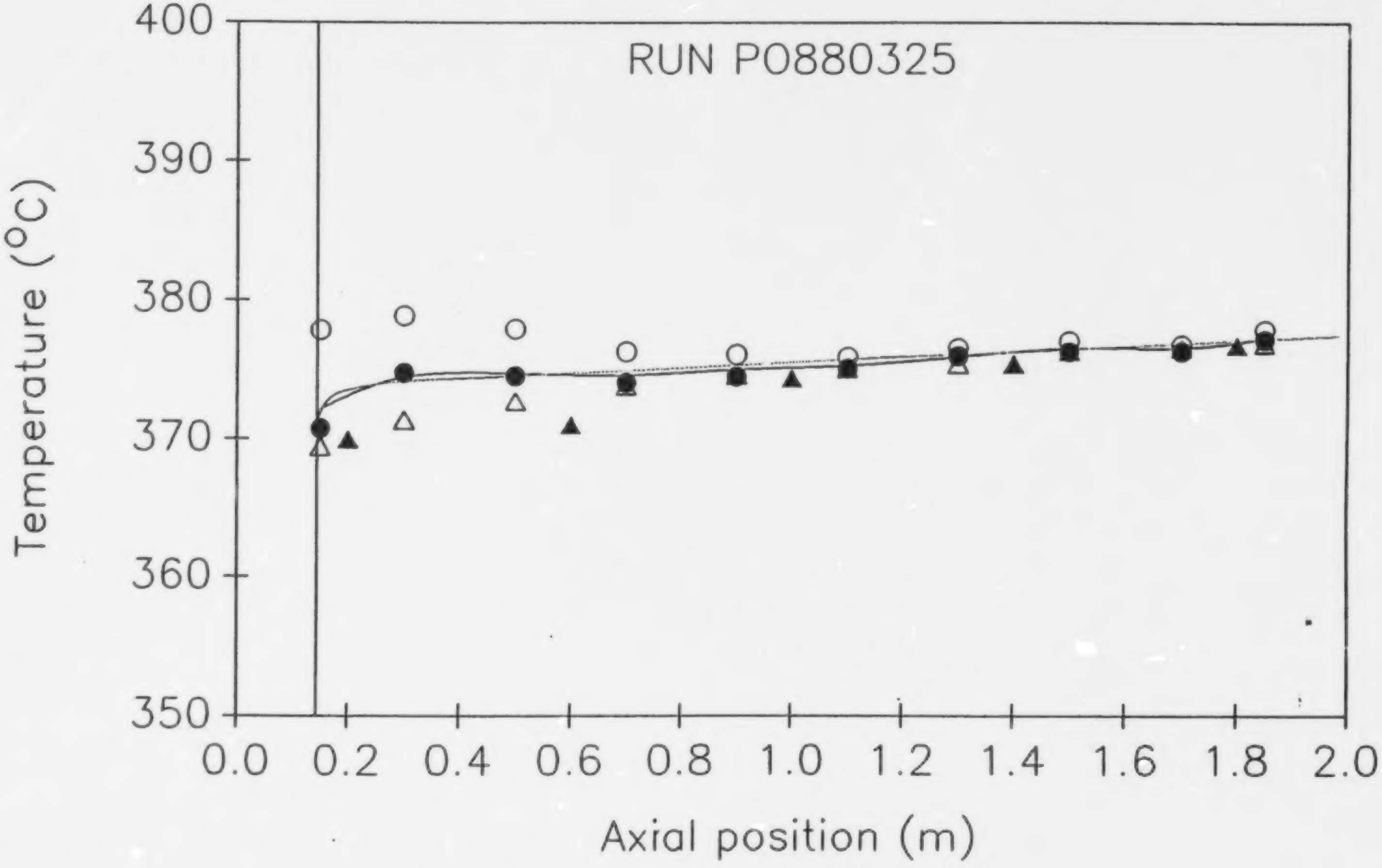


Figure 18-19: Revised temperature profile.

c. Deactivation

At regular periods, a run was repeated to assess the catalyst deactivation in the pilot unit. The runs were PO880203 (Time on stream, 20.5 hr), PO880212 (Time on stream, 42.2 hr), PO880308 (Time on stream, 68.7 hr) and PO880325 (Time on stream, 109 hr). The CO conversion which indicated the level of deactivation decreased rapidly at the beginning (50.3%-20.5hr to 41.2%-42.2hr). Then the rate of deactivation was much slower tending the activity towards a stable level at the end of the 19 runs (38.5%-68.7hr to 33.3%-109hr). The same observation was obtained with the productivity per tube and the yields. These productivities even increased for the final run. However the product distribution was not essentially affected by deactivation.

IV.E Simulation of the PO reactor.

a. Introduction

A computer program was developed in order to simulate the Pseudoadiabatic reactor using the bifunctional MSC + ZSM-5 catalyst. In this simulation the methanol synthesis, the methanol conversion (MTG) and the water-gas-shift reaction were taken into account. The kinetic model presented in a previous section of this report (section III.A.5) was used in the computer algorithm. In this kinetic model, it is considered that the controlling reaction is the methanol synthesis and the water-gas-shift reaction is at equilibrium.

The mathematical model used involved a pseudohomogeneous one dimensional representation of the catalytic bed. The set of equations for this model and the different assumptions are presented in Appendix K. Due to the lack of accuracy of the pre-exponential kinetic factor b, and the overall heat-transfer coefficient U, the use of a Marquardt optimization routine was combined with the numerical solution of the model. The results of the simulation were compared with the experimental data, and the values of b and U were modified until the best fitting numerical values were obtained. The fitting was based on the comparison of the experimental revised average temperature profile and measured outlet CO conversion with the average temperature profile and the outlet conversion predicted by the one-dimensional pseudohomogeneous model.

The simulation algorithm was implemented by means of a number of computer programs, written in FORTRAN 77 language, on a Hewlett-Packard 1000 series 600 A+ computer available in our laboratory.

The program consisted of two main routines: one was a fourth-order Runge-Kunta routine used to integrate the set of four differential equations and the second was the Marquardt optimization routine. The computer code called OPTI is presented in Appendix M. The printouts of the simulation results containing the optimized U and b values were obtained by means of the computer program SIMU presented in Appendix M.

The computer simulation allowed the calculation of CO and H_2 conversions, product distribution (CO, H_2, CO_2, H_2O, MeOH and HC) and average axial temperature profiles.

Furthermore, the heat of reaction was assessed by means of an overall enthalpy balance (computer program called ENTHALPY, presented in Appendix M). By knowing the flow rates of reactant and coolant, the physical properties of the streams, the inlet and outlet temperatures and the CO conversion, the heat of reaction was evaluated. The heat of reaction was defined as heat generated by unit mole of CO converted in methanol. Table 33 reports the calculated enthalpies of reaction. The enthalpies of reaction observed oscillate between -19000 and -59000 Kcal/Kmol. The average value is -34010 Kcal/Kmol and the standard deviation 10548 Kcal/Kmol. This average value was found to be much higher than the one calculated from the thermodynamic data which under the same conditions is around -20000 Kcal/Kmol. It has to be mentioned that this relatively large deviation of the enthalpy of reaction is the result of experimental errors in the coolant side temperatures.

b. Results

The temperature profiles, plotted in the x-T diagrams from the experimental measurements and the modelling, are reported in Figures 18-1 to 18-19. From these figures, it is possible to observe that the computer model with the optimize parameters predicted quite well the trends of the cross-section averaged temperature.

Furthermore, additional comparaisons of experimental vs theorical conversions are given on Table 34. The regimes obtained for these runs are also reported. As it is shown in this table, the model predicted well the type of operating regime for the catalytic reactor (PO: pseudoadiabatic for the temperatures, MFARP: non-pseudoadiabatic). However, since the one-dimensional model failed to generate the centerline temperature, it cannot differentiate well between PO and POAT.

Run	Heat of Reaction (kcal/kmol CO converted in MeOH)
P0880201	-30816.8
P0880203	-19278.4
P0880204	-28259.0
P0880208	-31257.2
P0880210	-26344.8
P0880212	-36239.2
P0880225	-30345.8
P0880302	-36898.8
P0880304	-36626.8
P0880307	-29820.0
P0880308	-47386.2
P0880309	-21362.2
P0880314	-32456.4
P0880316	-29669.2
P0880317	-35209.6
P0880318	-20041.2
P0880322	-59046.4
P0880323	-53652.6
P0880325	-41491.0

Table 33: Calculated Heat of Reaction

Run	Experimental Regime	Simulated Regime	Experimental CO conversion	Simulated CO conversion
P0880201	POAT[1]	PO	20.6	16.0
P0880203	POAT	PO	50.3	49.8
P0880204	POAT	PO	33.1	39.5
P0880208	MFARD[2]	PO	30.5	29.0
P0880210	POAT	PO	36.2	35.5
P0880212	POAT	PO	41.2	23.4
P0880225	POAT	PO	24.1	17.1
P0880302	POAT	PO	21.6	17.2
P0880304	POAT	PO	20.9	15.6
P0880307	POAT	PO	18.1	12.8
P0880308	POAT	PO	38.5	20.6
P0880309	POAT	PO	18.6	10.9
P0880314	PO[3]	PO	20.3	18.1
P0880316	MFRAD	PO	48.2	36.7
P0880317	POAT	PO	34.9	29.9
P0880318	POAT	PO	16.4	13.9
P0880322	MFRAD	PO	39.2	37.4
P0880323	MFRAD	PO	22.7	17.8
P0880325	POAT	PO	33.3	18.6

1 POAT : average temperature increasing with a small hot-spot in the relative temperature profile.
2 PO : all the temperature profiles increasing.
3 MFARD: non pseudoadiabatic.

Table 34: Experimental and predicted regimes and conversions

Another important observation was that the predicted outlet conversion values were, almost in all cases, somewhat lower than the experimental measured conversions. This can be explained considering the difficulties of predicting the enthalpy of reaction. As mentionned previouly in this report the enthalpy of reaction was in most cases higher than the ones calculated from thermodynamic data. If the enthalpy of reaction used is higher than the real one, the only possible way to calculate the right temperature profile is to decrease the rate of reaction. In the reactor simulation results, that can be achieved either by lowering the pre-exponential factor or/and simulating a lower conversion.

Table 35 listed the optimized b and U values as well as the U values calculated from correlations. As it can be observed in this table, the pre-exponential factor b shows a substantial variation (2.5-11.9). The average value is 6.86 and the standard deviation 2.88. The average value was in excellent agreement or slightly higher than the one obtained in the Berty reactor (6.01). It has to be pointed out that the pre-exponential factors in the simulation of the Pseudoadiabatic reactor included a contribution coming from the deactivation of the catalyst. As it is shown in the Table 35, there is no significative change of b from the first run to the last one, which means that the experimental error probably introduces higher variation than the contribution of the deactivation effect itself.

On the other side, the U values have an average value of 149.1 Kcal/-hr*m2*K with a standard deviation of 114.3 Kcal/hr*m2*K compared to the U values calculated from literature correlations (Froment and Bischoff (1979)) which gave an average of 210.8 Kcal/hr*m2*K with a standard deviation of 20 Kcal/hr*m2*K. Given litterature correlations for the heat transfer parameters have a intrinsic

Run	b	U	U correlation
P0880201	9.77	91.2	205.8
P0880203	7.65	103.8	199.7
P0880204	10.22	231.8	199.7
P0880208	6.21	123.9	202.1
P0880210	7.58	263.7	197.6
P0880212	2.87	75.8	199.7
P0880225	6.51	103.0	205.5
P0880302	6.06	113.7	205.4
P0880304	6.93	104.0	205.0
P0880307	8.35	106.2	206.1
P0880308	2.33	42.2	199.5
P0880309	11.00	89.4	206.6
P0880314	10.75	383.3	259.7
P0880316	4.69	126.4	200.3
P0880317	5.09	132.8	202.4
P0880318	11.00	100.6	204.6
P0880322	6.85	464.1	251.3
P0880323	7.54	483.8	255.3
P0880325	2.50	51.3	200.2

Table 35: Optimized b and U values

error of about 50%, the optimize U values obtained were considered as acceptable in the context of the present study.

In summary, the discrepancies between experimental and modelling results can be mainly explained by experimental errors on the temperature measurement. This is particularly true at the top of the bed where an error of 2 or more degrees can be easily obtained. Also, the heaters, which maintain the reactor at operating temperature, can prone a considerable inaccuracy in the measurement of the coolant temperature, which have a large effect on the parameter such as the heat of rection derived from the overall enthalpy balance .

Also other experimental errors like flow and pressure adjustment and catalyst distribution in the bed could have induced errors in the simulation.

In summary, the present results show promising possibilities for the Pseudoadiabatic Operation. It is proposed however to investigate further the impact of possible errors (temperatures, catalyst distribution) questions during the new phase of research in order to achieve a stringent test of the proposed model and an accurate determination of various kinetic and thermal parameters (heat transfer coefficient, pre-expenential factor, heat of reaction).

SECTION V

Conclusion

CONCLUSION

This final report highlights the major achievements of this program:

1. A bi-functional catalyst was successfully developed at the University of Western Ontario with the dual function of methanol synthesis and methanol conversion. This catalyst demonstrated very high selectivity for aromatics hydrocarbons while producing little amount of methane. The catalyst also induced water-gas-shift reaction resulting in a production of carbon dioxide. It was shown that the adequate catalyst formulation and catalyst pretreatment were key factors for the adequate operation of these dual catalysts. For the methanol synthesis function of this catalyst two techniques of preparation (wet and co-precipitation methods) were tested. Furthermore, the adequate formulation was selected by means of a significant number of screening reaction runs performed in a Berty well mixed reactor unit.

2. The bi-functional catalyst was characterized using XRD and BET. Some valuable insights were obtained about the states of the zinc and chrome as well as on the role of the oxides of these two metals.

3. A valuable kinetic model was developed for methanol conversion on ZSM5 zeolite. Following this task a second kinetic model was proposed for the conversion of synthesis gas into liquid hydrocarbons in the bifunctional catalyst. The transformation of synthesis gas takes place on the dual MSC/ZSM-5 catalyst with a "drain-off" effect, e.g. methanol is formed and readily converted on the zeolite component. The kinetic model developed for

the bifunctional catalyst was tested with experimental data obtained in a Berty well-mixed reactor. The analysis was complemented with the determination of the kinetic parameters using a Marquardt non-linear regression technique.

4. An additional number of runs was conducted in the Berty well-mixed reactor, as part of the activities planned for this contract, with two catalysts provided by CANMET. One of them (CANMET Sample Code 102) showed no significant catalytic activity. The runs were then, devoted to test the second sample (CANMET Sample Code 112). It was observed that the CANMET-112 catalyst showed a Schulz-Flory-Anderson product distribution (significant fraction of light hydrocarbons), that ressembled a Fischer-Tropsch catalyst.

5. The pilot plant unit used extensively at the Chemical Reactor Engineering Centre, University of Western Ontario, in a previous project, for the conversion of methanol was modified and adapted for the conversion of synthesis gas. This included the construction of a new reactor to operate at higher pressures and temperatures, the replacement of the feeding lines with the needed accesories and flow controllers, the modification of the product recovery system and several improvements introduced in the insulation of the unit and temperature monitoring at various strategic locations in the reactor.

6. A number of runs were developed in the pilot plant unit to confirm the possible application of the novel Pseudoadiabatic Reactor concept for the selective conversion of synthesis gas into hydrocarbons (gasoline range).

This reactor concept, developed in our laboratory and successfully tested for the methanol-to-gasoline reaction (MTG), provides a gradual increase in the axial temperature in a cocurrently cooled packed-bed catalytic reactor.

It was observed in this study that the Pseudoadiabatic Operation was obtained consistently for most of the runs. Even for the non-Pseudoadiabatic conditions the measured hot-spots were very attenuated and close to the limiting conditions for the Pseudoadiabatic regime.

Another finding of particular interest was the CO converted into liquid hydrocarbons that ranged between 12 to 17% and the fraction of C_5^+ hydrocarbons that in some of the runs reached values as high as 70% of the total hydrocarbons produced. Methane fraction was also found to be very low. It should also be pointed out that during the runs in the pilot plant unit some valuable observations were performed concerning catalyst deactivation. It was demonstrated that a relatively quick deactivation was followed by a condition were catalyst activity was stabilized.

In summary, the obtention of the Pseudoadiabtic regime and the high selectivity to aromatics support the possible application of the PO approach to the design and engineering of this synthesis gas conversion reactor.

A process based on a bifunctional catalyst and a multitubular Pseudoadiabatic reactor will also represent important capital and operating cost savings with respect to the three conversion stages (methanol synthesis, methanol dehydratation, dimethylether conversion) proposed in the synthesis, methanol dehydratation, dimethylether conversion) proposed in the Mobil process in New Zealand. Besides, a steam reformer producing synthesis gas from methane with CO/H_2 ratio of 1 instead of 2 or 3 would reduce significantly the investment and operating cost for this unit (Teuner, 1987; Goff et al., 1987; Dibbern et al., 1986). In the process, the carbon dioxide produced by water-gas-shift (see conclusion 1) in the Pseudoadiabatic reactor will be recycled back to the natural gas steam reforming unit. In this way synthesis gas mixture (CO/H2=1) will be obtained without carbon losses for the process.

7. The present program also involved significant activities in the area of reactor modelling. It was observed that the predictions of reactor regime (Pseudoadiabatic, non-Pseudoadiabatic) using the kinetic model for the bi-functional catalyst and the computer algorithms, previously developed at the University of Western Ontario, confirmed experimental observations in the pilot plant. It was also found that the average value of the kinetic pre-exponential constant, derived by non-linear regression techniques, were consistent with the values obtained in independant experiments in the well mixed Berty reactor. Futhermore, it was also found that other very important parameter for reactor design and operation, the overall heat transfer coefficient was in the range of the values reported in the literature with a general trend, however, towards lower levels.

Finally it has to be stated that the results of the present contract while confirming the value and potential of the Pseudoadiabatic Reactor for the selective conversion of synthesis gas into hydrocarbons using a bi-functional catalyst in a single reactor, operating at moderate pressure, provide a most valuable basis for further research. For example, it can be concluded that improvements are needed in the methods for determining and predicting heat of reactions closely related to further refinements on temperature monitoring in the coolant fluid jacket. Moreover, further ameliorations of the catalyst formulation are required to increase the productivity of liquid hydrocarbons and to successfully commercialize this process.

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REFERENCES

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APPENDIX A

Method for the synthesis of the ZSM-5 Zeolite

Method for the synthesis of the HZSM-5 Zeolite (MZ-1)

1) REACTANTS

- The silica (SiO_2) source was a sodium silicate commonly commercialized as "Waterglass" and provided by Lawrason, under the name N-Silicate of soda. Its composition by weight was: 28.7% SiO_2, 8.9% Na_2O, 62.4% H_2O.
- The aluminum source was aluminum sulfate $Al_2(SO_4)3.17H_2O$ provided by Fischer.
- The organic base was tetrapropylammonium bromide (TPABr) provided by BDH.
- Sodium chloride, ACS reagent, provided by BDH.
- Sulfuric acid, ACS reagent, provided by Fisher.

2) PREPARATION OF GEL

The procedure involved the following steps:

a) Preparation of a basic solution (solution A) from 4804 g of sodium silicate in 2285 ml of water.

b) Preparation of an acidic solution (solution B) from 302.7 g of aluminum sulfate, 1884 ml of water, 241.4 ml of sulfuric acid and (after cooling) 571.3 g of TPABr.

c) Preparation of a solution (Solution c) of 647.4 g of NaCl in 1860 ml of water.

d) Solutions A and B were poured simultaneously into solution c, while stirring and maintaining the pH between 2 and 4. When all solution B was utilized, approximately half of solution A was still left. The vessel used for this purpose was a 12 litres stainless steel autoclave, equipped with two coaxial marine propeller stirrers and jacket heaters.

e) Stirring was maintained for 2 hours at room temperature.

f) The remaining solution A was then poured, and the pH allowed to raise to 10.

g) Once exhausted solution A, reaction is carried out at room temperature for another 2 hours, while stirring was maintained.

h) The autoclave was sealed, the temperature brought up to 160°C and the stirring speed set at 200-300 rpm. Autogenous pressure of approximately 100 PSI developed under these conditions.

i) Conditions described in step h were maintained for 7 days. This period was generally enough to allow complete crystallization of the gel. After this period, HZSM-5 crystal were deposited at the bottom, leaving a clear surnatant.

3) WASHING OF THE PRECURSOR

1537 g of precursor were recovered by filtration from the mother liquor at a pH of 10.8. The clusters of zeolite were crushed very easily in fine powder, and washed twice with 135 and 70 litres of water at 70°C, at a pH of about 8.

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a) Preparation of a basic solution (solution A) from 4804 g of sodium silicate in 2285 ml of water.

b) Preparation of an acidic solution (solution B) from 302.7 g of aluminum sulfate, 1884 ml of water, 241.4 ml of sulfuric acid and (after cooling) 571.3 g of TPABr.

c) Preparation of a solution (Solution c) of 647.4 g of NaCl in 1860 ml of water.

d) Solutions A and B were poured simultaneously into solution c, while stirring and maintaining the pH between 2 and 4. When all solution B was utilized, approximately half of solution A was still left. The vessel used for this purpose was a 12 litres stainless steel autoclave, equipped with two coaxial marine propeller stirrers and jacket heaters.

e) Stirring was maintained for 2 hours at room temperature.

f) The remaining solution A was then poured, and the pH allowed to raise to 10.

g) Once exhausted solution A, reaction is carried out at room temperature for another 2 hours, while stirring was maintained.

h) The autoclave was sealed, the temperature brought up to 160°C and the stirring speed set at 200-300 rpm. Autogenous pressure of approximately 100 PSI developed under these conditions.

i) Conditions described in step h were maintained for 7 days. This period was generally enough to allow complete crystallization of the gel. After this period, HZSM-5 crystal were deposited at the bottom, leaving a clear surnatant.

3) WASHING OF THE PRECURSOR

1537 g of precursor were recovered by filtration from the mother liquor at a pH of 10.8. The clusters of zeolite were crushed very easily in fine powder, and washed twice with 135 and 70 litres of water at 70°C, at a pH of about 8.

APPENDIX B

CONVERSION OF METHANOL TO GASOLINE:

- calculation of conversions, mass balances and of the weight and molar product distributions.
- Listing of program MTGPROD
- Listing of subroutine DATAIN
- Result printout (for Run MTG 2c)

```
ftn 7x,l,s
$files 0,8
      PROGRAM MTGPROD
C ***************************************************************************
C          CALCULATION OF WEIGHT AND MOLAR DISTRIBUTIONS OF THE
C          PRODUCTS FOR THE METHANOL TO GASOLINE REACTION
C
C    RUNPARAM              : file, created with  the program  DATAIN, where  the
C     ('RUNPARAM@.DAT')  run parameters are stored.
C    GASCOMP               : file of the cleaned ( corrected for the  extra  and
C     ('GASCOMP@.DAT')   missing peaks to match  the number of compounds ex-
C                        pected, N ) weight composition of the gas fraction,
C                        created from  the GC analysis  of the non-condensed
C                        product fraction.
C    LIQCOMP               : the same as for GASCOMP, but for  the liquid hydro-
C     (;LIQCOMP@.DAT')   carbon phase.
C    'MTGPRODNAME.DAT' : list of  the name of  the compounds of  the product
C                        distribution, in the order of appearance in  the GC
C                        analysis.
C    'MTGLUMPNAME.DAT' : list  of  the  name of  the lumped  species  in the
C                        hydrocarbon distribution.
C    'MTGMOLEWEIGHT.DAT': list of  the molecular weight of  each compound of
C                         the product  distribution, in  the order of appea-
C                         rance in the GC analysis.
C    'MTGCNUM.DAT': list of  the number of  carbon in  each compound of  the
C                   product distribution, in the order of appearance in  the
C                   analysis.
C    OUTPUTFILE   : file where molar product distribution and run parameters
C     ('MTG@.DAT')  are stored, for the kinetic study.
C
C ********************** Copyright 1987 A. Mahay *************************
C
       CHARACTER*5 RN ,SRN*10
       CHARACTER *16 RUNPARAM,LIQCOMP,GASCOMP,OUTPUTFILE
       DIMENSION WLHCR(150), WLHC(150),WGR(150),WG(150),WPC(150)
       DIMENSION THC(150),TLHC(150),SLLHC(150)
       INTEGER PM(150),CN(150),IPAR(41),IOL(46),IAR(16)
       REAL MLHC(150),MG(150),MPC(150),LLHC(50)
       REAL MHC,LHC,MET,MGT,MBO,MBC,MT,IFR,MFR,LHCPC,LAR
       CHARACTER NAME(150)*50,LNAME(12)*40,LHCNAME(44)*30,LLNAME(11)*40
       DATA IPAR/12,13,15,19,20,21,23,29,31,34,35,36,37,38,41,44,47,49,
      $54,55,56,57,58,59,60,61,63,64,70,73,78,79,81,82,83,90,91,97,101,
      $102,104/
       DATA IOL/14,16,17,18,22,24,25,26,27,28,30,32,33,39,40,42,43,45,
      $46,48,51,52,53,62,65,66,67,68,69,71,72,75,77,84,85,86,87,88,89,
      $93,96,98,99,103,105,107/
       DATA IAR/50,74,76,80,92,94,95,100,106,108,109,110,111,112,113,
      $114/
       DATA (LNAME(I), I=6,12) /'i-Butane','n-Butane','Butenes',
      $'Paraffins + Cycloparaffins','Olefins + Cycloolefins',
      $'Aromatics','C11+'/
       DATA LLNAME /'C2-C3','C4 Paraffins','C4 Olefins',
      $'C5-C9 Paraffins + Cycloparaffins','C5-C9 Olefins + Cycloolefins'
      $,'C10+ P+O+N','Toluene','C8 Aromatics','C9 Aromatics',
      $'C10 Aromatics','C11+ Aromatics'/
      WRITE(1,*)'ENTER # OF THE RUN'
      READ(1,'(A5)') RN
      IEND=INDEX(RN,' ')
      SRN=RN(1:IEND-1) // '.DAT'
      RUNPARAM='RUNPARAM' // SRN
      LIQCOMP='LIQCOMP' // SRN
      GASCOMP='GASCOMP' // SRN
      OUTPUTFILE = 'MTG' // SRN
      OPEN(10,FILE=RUNPARAM)
      READ(10,*) N
C
C
C             DATA TRANSFER
C
      READ(10,*)CW
      READ(10,*)BT,P
      READ(10,*)IFR,MFR
      READ(10,*)FMET
      READ(10,*)T
      READ(10,*)FR
      READ(10,*)LHC,AF
      READ(10,*)RT
      READ(10,*)CFDMEL,CFDMEG
      READ(10,*)WCM1,ACM1,WCM2,ACM2
      READ(10,*)AAF
      CLOSE(10)
      WRITE (1,*) 'First file OK !'
      OPEN(20,FILE='MTGMOLEWEIGHT.DAT')
      READ(20,*) (PM(I), I=1,N)
      CLOSE(20)
      write (1,*) 'Second file OK !'
      OPEN(30,FILE='MTGPRODNAME.DAT')
      READ(30,*) (NAME(I), I=1,N)
      CLOSE(30)
      write (1,*) 'Third file OK'
      OPEN(40,FILE='MTGCNUM.DAT')
      READ(40,*) (CN(I), I=1,N)
      CLOSE(40)
      write (1,*) 'Fourth file OK !'
      OPEN(50,FILE=LIQCOMP)
      READ(50,*) (WLHCR(I), I=1,N)
      CLOSE(50)
      write (1,*) 'Fifth file OK !'
      OPEN(60,FILE=GASCOMP)
      READ(60,*) (WGR(I), I=1,N)
      CLOSE(60)
      write (1,*) 'Sixth file OK !'
      OPEN(65,FILE='MTGLUMPNAME.DAT')
      READ(65,*) (LHCNAME(I), I=1,44)
      CLOSE(65)
      write (1,*) 'Seventh file OK!'
C
C *****************LIQUID HYDROCARBON COMPOSITION**********************
C
      WLHCR(6)=WLHCR(6)*CFDMEL
      SWLHC=0.
      DO 100 I=1,N
      SWLHC=SWLHC+WLHCR(I)
  100 CONTINUE
      DO 110  I=1,N
      WLHC(I)=100*WLHCR(I)/SWLHC
  110 CONTINUE
C
C***********************GASEOUS PRODUCT COMPOSITION**********************
C
C***************number of moles of gaseous products*********************
C
      MGT=FR*T/(82.05*(273.15+RT))
C
C***************average molecular weight of the gaseous fraction********
C                                  ( AMWG )
C
      WGR(6)=WGR(6)*CFDMEG
      SWG=0
      DO 120 I=1,N
      SWG=SWG+WGR(I)
  120 CONTINUE
      DO 130 I=1,N
      WG(I)=100*WGR(I)/SWG
  130 CONTINUE
      TMG=0
      DO 140 I=1,N
      TMG=TMG+WG(I)/PM(I)
  140 CONTINUE
      AMWG=100/TMG
C
C****************weight of the gaseous fraction (grams)*****************
C
      GPR=AMWG*MGT
C
C*************************AQUEOUS FRACTION*******************************
C  AF: mass of aqueous fraction; MET: mass of methanol; WAT: mass of water
C
      WM=WCM1+(WCM2-WCM1)*(AAF-ACM1)/(ACM2-ACM1)
      MET=WM*AF/100
      WAT=AF-MET
C
C********************MASS BALANCE ON OXYGEN******************************
C
      MBO=(WAT/18+MET/32+(WLHC(6)*LHC+WG(6)*GPR)/46/100)*16 - FMET/2
C
C***************MASS DISTRIBUTION(WT%) OF PRODUCTS ( WPC )**************
C
      PROD=AF+LHC+GPR
      DO 150 I=1,N
      WPC(I)=(WLHC(I)*LHC+WG(I)*GPR)/PROD
  150 CONTINUE
      WPC(131)=WPC(131)+100*MET/PROD
      WPC(132)=WPC(132)+100*WAT/PROD
C
```

```
C***********************MASS BALANCE ON CARBON ( MBC )******************
C
      C=0
      DO 160 I=1,N
      C=C+WPC(I)*PROD*CN(I)/PM(I)/100
  160 CONTINUE
      C=C*12
      MBC=C-FMET*12/32
C
C******************MOLAR DISTRIBUTION OF PRODUCTS ( MPC )***************
C
      PMS=0
      DO 170 I=1,N
      PMS=PMS+WPC(I)/PM(I)
  170 CONTINUE
      MT=PMS*PROD/100
      DO 180 I=1,N
      MPC(I)=100*WPC(I)/PM(I)/PMS
  180 CONTINUE
C
C***********************RESULT PRINTING*********************************
C
      OPEN(70,FILE=OUTPUTFILE)
      WRITE(70,*)N
      WRITE(6,500) RN
  500 FORMAT(/,30X,'PRODUCT DISTRIBUTION OF RUN MTG',A3,///)
      WRITE(6,510)CW
  510 FORMAT(1X,'CATALYST WEIGHT=',F7.2,1X,'GRAMS',/)
      WRITE(6,520)BT
  520 FORMAT(1X,'BED TEMPERATURE=',F5.0,1X,'C')
      WRITE(6,530)P
  530 FORMAT(1X,'PRESSURE IN THE REACTOR=',F6.2,1X,'PSIG')
      WRITE(6,540)MFR
  540 FORMAT(1X,'METHANOL FLOW RATE=',F7.5,1X,'MOLES/MIN'/)
      WRITE(6,550)IFR
  550 FORMAT(1X,'INERT FLOW RATE=',F7.1,1X,'STP ML/MIN'/)
      WRITE(6,560)FMET
  560 FORMAT(1X,'MASS OF METHANOL FED=',F7.2,'GRAMS'/)
      WRITE(6,570)T
  570 FORMAT(1X,'RUN TIME=',F5.0,'MIN'/)
      WRITE(6,572) MBO
  572 FORMAT(1X,'MASS BALANCE ON OXYGEN =',F5.2,'GRAMS'/)
      WRITE(6,574) MBC
  574 FORMAT(1X,'MASS BALANCE ON CARBON =',F5.2,'GRAMS'/)
C
C****************bulk product mass distribution*************************
C
      LHCPC=(100-WLHC(6))*LHC/PROD
      GHCPC=(100-WG(6))*GPR/PROD
      WRITE(6,580)
  580 FORMAT(//18X,5'*','BULK PRODUCT MASS DISTRIBUTION(WT%)',5'*',/)
      WRITE(6,590)
  590 FORMAT(5X,'LIQ HC',8X,'GASEOUS HC',10X,'DME',12X,'WATER',11X,
     1'METOH'/)
      WRITE(6,600) LHCPC,GHCPC,WPC(6),WPC(132),WPC(131)
  600 FORMAT(5X,4(F6.2,10X),F6.2//)
C
      WRITE(6,610)PROD
  610 FORMAT(1X,'TOTAL MASS PRODUCT=',F6.2,1X,'GRAMS'/)
      WRITE(6,620)AMWG
  620 FORMAT(1X,'AVERAGE MOLECULAR WEIGHT OF GAS PRODUCTS=',F5.1,1X,
     1'GRAM/MOLE'/)
      WRITE(6,630)MT
  630 FORMAT(1X,'TOTAL NUMBER OF MOLES IN PRODUCTS=',F6.3,1X,'MOLES'/)
      WRITE(6,640)
  640 FORMAT(///,25X,5'*','PRODUCT DISTRIBUTION',5'*',//)
      WRITE(6,650)
  650 FORMAT(1X,'NUMBER',25X,'NAME',26X,'MASS %',2X,'MOLE %'//)
      DO 660 I=1,N
      WRITE(6,670)I,NAME(I),WPC(I),MPC(I)
  670 FORMAT(3X,I3,1X,A50,2X,F7.3,2X,F7.3)
      WRITE(70,*) WPC(I),MPC(I)
  660 CONTINUE
      WRITE(70,*)CW
      WRITE(70,*) BT,P
      WRITE(70,*) MFR,IFR
      WRITE(70,*) MT,T
      WRITE(70,*)PROD
      WRITE(70,*)MBO,MBC
      WRITE(70,*)RT
      CLOSE(70)
C
C******LIQUID,GAS AND TOTAL HYDROCARBON MASS PRODUCT DISTRIBUTIONS******
      WRITE(6,671)
  671 FORMAT(//,6X,3'*','LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUT
     $IONS',3'*',//)
      WRITE(6,672)
  672 FORMAT(1X,'NUMBER',13X,'NAME',12X,'LIQ HC %',2X,'GASEOUS HC %',
     $2X,'TOTAL HC %',//)
      FAC1=100-WPC(6)-WPC(131)-WPC(132)
      FAC2=100-WLHC(6)-WLHC(131)-WLHC(132)
      FAC3=100-WG(6)-WG(131)-WG(132)
      DO I=1,N
      THC(I)=100*WPC(I)/FAC1
      WLHC(I)=100*WLHC(I)/FAC2
      WG(I)=100*WG(I)/FAC3
      END DO
      THC(6)=0
      WLHC(6)=0
      WG(6)=0
      THC(131)=0
      WLHC(131)=0
      WG(131)=0
      THC(132)=0
      DO I=1,N
      WRITE(6,674) I,NAME(I),WLHC(I),WG(I),THC(I)
      END DO
  674 FORMAT(3X,I3,1X,A31,1X,F7.4,5X,F7.4,6X,F7.4)
C
C************LUMP TOTAL HYDROCARBON MASS DISTRIBUTION******************
```

```
C
      DO I=1,5
      TLHC(I)=WPC(I)
      LNAME(I)=NAME(I)
      END DO
      TLHC(6)=WPC(7)
      TLHC(7)=WPC(9)
      TLHC(8)=WPC(8)+WPC(10)+WPC(11)
      TLHC(9)=0
      DO I=1,41
      J=IPAR(I)
      TLHC(9)=TLHC(9)+WPC(J)
      END DO
      TLHC(10)=0
      DO I=1,46
      J=IOL(I)
      TLHC(10)=TLHC(10)+WPC(J)
      END DO
      TLHC(11)=0
      DO I=1,16
      J=IAR(I)
      TLHC(11)=TLHC(11)+WPC(J)
      END DO
      TLHC(12)=0
      DO I=115,130
      TLHC(12)=TLHC(12)+WPC(I)
      END DO
C
      DO I=1,12
      TLHC(I)=100*TLHC(I)/(100-WPC(6)-WPC(131)-WPC(132))
      END DO
C
C**********LUMPED LIQUID HYDROCARBON COMPOSITION*************************
C
      LLHC(1)=WLHC(1)+WLHC(2)+WLHC(3)
      LLHC(2)=WLHC(5)
      LLHC(3)=WLHC(4)
      LLHC(4)=WLHC(9)
      LLHC(5)=WLHC(7)
      LLHC(6)=WLHC(8)+WLHC(10)+WLHC(11)
      LLHC(7)=WLHC(15)
      LLHC(8)=WLHC(12)
      LLHC(9)=WLHC(14)+WLHC(16)+WLHC(17)+WLHC(18)
      LLHC(10)=WLHC(13)
      LLHC(11)=WLHC(21)
      LLHC(12)=WLHC(20)+WLHC(23)+WLHC(31)
      LLHC(13)=WLHC(19)
      LLHC(14)=WLHC(22)+WLHC(30)
      DO I=24,28
      LLHC(14)=LLHC(14)+WLHC(I)
      END DO
      LLHC(15)=WLHC(29)
      LLHC(16)=WLHC(32)
      LLHC(17)=WLHC(41)
      LLHC(18)=WLHC(34)+WLHC(35)
      LLHC(19)=WLHC(33)+WLHC(39)+WLHC(40)+WLHC(42)+WLHC(43)+WLHC(45)+
     $WLHC(46)
      LLHC(20)=WLHC(36)+WLHC(37)+WLHC(38)
      LLHC(21)=WLHC(53)
      LLHC(22)=WLHC(64)
      LLHC(23)=WLHC(54)+WLHC(55)+WLHC(57)
      LLHC(24)=WLHC(62)+WLHC(65)+WLHC(66)+WLHC(67)+WLHC(68)+WLHC(87)+
     $WLHC(99)
      LLHC(25)=WLHC(44)+WLHC(47)+WLHC(49)+WLHC(56)+WLHC(58)+WLHC(59)+
     $WLHC(60)+WLHC(61)+WLHC(63)+WLHC(70)
      LLHC(26)=WLHC(48)+WLHC(51)+WLHC(52)+WLHC(69)+WLHC(71)+WLHC(72)+
     $WLHC(98)
      LLHC(27)=WLHC(97)
      LLHC(28)=WLHC(78)+WLHC(79)
      LLHC(29)=WLHC(73)+WLHC(81)+WLHC(82)+WLHC(83)+WLHC(90)
      LLHC(30)=WLHC(75)+WLHC(77)+WLHC(84)+WLHC(85)+WLHC(86)+WLHC(88)+
     $WLHC(89)+WLHC(93)+WLHC(96)
      LLHC(31)=WLHC(91)+WLHC(101)+WLHC(102)+WLHC(103)+WLHC(104)+
     $WLHC(105)+WLHC(107)+WLHC(123)
      LLHC(32)=WLHC(50)
      LLHC(33)=WLHC(74)
      LLHC(34)=WLHC(76)
      LLHC(35)=WLHC(80)
      LLHC(36)=WLHC(100)
      LLHC(37)=WLHC(94)+WLHC(95)
      LLHC(38)=WLHC(92)
      LLHC(39)=WLHC(108)
      LLHC(40)=WLHC(109)+WLHC(110)
      LLHC(41)=WLHC(106)+WLHC(112)
      LLHC(42)=WLHC(111)+WLHC(113)+WLHC(114)
      LLHC(43)=WLHC(126)
      DO I=115,119
      LLHC(43)=LLHC(43)+WLHC(I)
      END DO
      LLHC(44)=WLHC(120)+WLHC(121)+WLHC(122)+WLHC(124)+WLHC(125)
C
      DO I=1,44
      LLHC(I)=100*LLHC(I)/(100-WLHC(6)-WLHC(131)-WLHC(132))
      END DO
C
C*********SUMMARY OF LIQUID HYDROCARBON LUMPED COMPOSITION*************
C
      SLLHC(1)=LLHC(1)+LLHC(2)+LLHC(3)
      SLLHC(2)=LLHC(4)+LLHC(5)
      SLLHC(3)=LLHC(6)
      SLLHC(4)=LLHC(7)+LLHC(8)+LLHC(10)+LLHC(11)+LLHC(12)+LLHC(13)+
     $LLHC(15)+LLHC(17)+LLHC(18)+LLHC(20)+LLHC(22)+LLHC(23)+LLHC(25)+
     $LLHC(27)+LLHC(28)+LLHC(29)
      SLLHC(5)=LLHC(9)+LLHC(14)+LLHC(16)+LLHC(19)+LLHC(21)+LLHC(24)+
     $LLHC(26)+LLHC(30)
      SLLHC(6)=LLHC(31)
      SLLHC(7)=LLHC(32)
      SLLHC(8)=LLHC(33)+LLHC(34)+LLHC(35)
      SLLHC(9)=LLHC(36)+LLHC(37)+LLHC(38)
      SLLHC(10)=LLHC(39)+LLHC(40)+LLHC(41)+LLHC(42)
      SLLHC(11)=LLHC(43)+LLHC(44)
      LAR=0
      DO I=7,11
      LAR=LAR+SLLHC(I)
      END DO
C
C*******************PRINTING OF TABLES OF LUMPED DISTRIBUTIONS**********
C
      WRITE(6,680)
  680 FORMAT(//,10X,5'*','LUMPED LIQUID HYDROCARBON MASS DISTRIBUTION',
     $5'*',/)
      WRITE(6,682)
  682 FORMAT(1X,'COMPOUND',24X,'WEIGHT % OF LIQUID HYDROCARBONS',//)
      DO I=1,44
      WRITE(6,684) LHCNAME(I),LLHC(I)
      END DO
  684 FORMAT(1X,A30,13X,F6.2)
C
      WRITE(6,690)
  690 FORMAT(//,8X,5'*','SUMMARY TABLE OF LIQUID HYDROCARBON COMPOSITION
     $',5'*',/)
      WRITE(6,692)
  692 FORMAT(1X,'COMPOUND',31X,'WEIGHT % OF LIQUID HYDROCARBONS',//)
      DO I=1,11
      WRITE(6,694) LLNAME(I),SLLHC(I)
      END DO
  694 FORMAT(1X,A40,11X,F7.2)
C
      WRITE(6,700)
  700 FORMAT(//,10X,5'*','LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION',
     $5'*',/)
      WRITE(6,702)
  702 FORMAT(1X,'COMPOUND',31X,'WEIGHT % OF TOTAL HYDROCARBONS',//)
      DO I=1,8
      WRITE(6,710) LNAME(I),TLHC(I)
      END DO
      WRITE(6,704)
  704 FORMAT(/,1X,'C5+ HYDROCARBONS',/)
      DO I=9,12
      WRITE(6,710) LNAME(I),TLHC(I)
      END DO
  710 FORMAT(1X,A40,12X,F7.2)
C
      STOP
      END
```

```
FTN7X,L,S
$FILES 0,1
      PROGRAM  DATAIN
C*******************************************************************************
     This program creates a datafile  RUNPARAM@.DAT where the MTG run para-
     meters are stored.  This file is used in  MTGPROD.  ( @ stands for the
     run id).
     The runstring is:       Datain Runparam@.dat
C
C******************* Copyright A. Mahay 1987 ***********************************
C
      CHARACTER*16 OUTPUTFILE
      REAL IFR,MFR,LHC
      CALL FPARM(OUTPUTFILE)
      OPEN(10,FILE=OUTPUTFILE)
      WRITE( 1,*)'ENTER NUMBER OF COMPOUNDS IN THE  PRODUCTS'
      READ *,N
      WRITE(10,*)N
      WRITE(1,*)'ENTER CATALYST WEIGHT (GRAMS)'
      READ*,CW
      WRITE(10,*)CW
      WRITE(1,*)'ENTER BED TEMPERATURE (DEGREE C),
     1REACTOR PRESSURE (PSIG)'
      READ*,BT,P
      WRITE(10,*) BT,P
      WRITE(1,*)'ENTER INERT FLOW RATE(STP MIL/MIN),
     1METHANOL FLOW RATE (MOLE/MIN)'
      READ*,IFR,MFR
      WRITE(10,*)IFR,MFR
      WRITE(1,*)'ENTER MASS OF METHANOL FED(GRAMS)'
      READ*,FMET
      WRITE(10,*)FMET
      WRITE(1,*)'ENTER RUN TIME(MIN)'
      READ*,T
      WRITE(10,*)T
      WRITE(1,*)'ENTER GASEOUS PRODUCT TOTAL FLOW RATE(STP ML/MIN)'
      READ*,FR
      WRITE(10,*)FR
      WRITE(1,*)'ENTER WEIGHT OF LIQUID HC,WEIGHT OF AQUEOUS FRACTION
     1(GRAMS)'
      READ*,LHC,AF
      WRITE(10,*)LHC,AF
      WRITE(1,*)'ENTER ROOM TEMPERATURE(DEGREE C)'
      READ*,RT
      WRITE(10,*)RT
      WRITE(1,*)'ENTER CORRECTION FACTORS FOR DIMETHYLETHER IN LIQUID
     1HC GC ANALYSIS,IN GASEOUS PRODUCT GC ANALYSIS'
      READ*,CFDMEL,CFDMEG
      WRITE(10,*)CFDMEL,CFDMEG
      WRITE(1,*)'ENTER WT% METOH,AREA% METOH IN CALIBRATION MIXTURE 1,
     1WT% METOH,AREA% METOH IN CALIBRATION MIXTURE 2(GC-TCD ANALYSIS)'
      READ*,WCM1,ACM1,WCM2,ACM2
      WRITE(10,*)WCM1,ACM1,WCM2,ACM2
      WRITE(1,*)'ENTER AREA% OF METHANOL IN AQUEOUS FRACTION
     1(GC-TCD ANALYSIS)'
```

```
READ*,AAF
WRITE(10,*)AAF
CLOSE(10)
STOP
END
```

```
                         PRODUCT DISTRIBUTION OF RUN MTG2c


CATALYST WEIGHT=  10.70 GRAMS

BED TEMPERATURE= 339. C
PRESSURE IN THE REACTOR=  2.00 PSIG
METHANOL FLOW RATE= .00250 MOLES/MIN

INERT FLOW RATE=    0.0 STP ML/MIN

MASS OF METHANOL FED=  10.88GRAMS

RUN TIME= 127.MIN

MASS BALANCE ON OXYGEN = -.11GRAMS

MASS BALANCE ON CARBON = -.36GRAMS


               *****BULK PRODUCT MASS DISTRIBUTION(WT%)*****

   LIQ HC          GASEOUS HC          DME           WATER          METOH

    15.58            22.79             .93           53.72           6.97

TOTAL MASS PRODUCT= 10.33 GRAMS

AVERAGE MOLECULAR WEIGHT OF GAS PRODUCTS= 46.9 GRAM/MOLE

TOTAL NUMBER OF MOLES IN PRODUCTS=  .398 MOLES


                    *****PRODUCT DISTRIBUTION*****

NUMBER                       NAME                           MASS %  MOLE %


    1  Methane                                               .221    .358
    2 Ethylene                                              4.263   3.951
    3 Ethane                                                 .047    .041
    4 Propylene                                             1.951   1.206
    5 Propane                                               3.228   1.904
    6 Dimethylether                                          .928    .524
    7 i-Butane                                              4.424   1.980
    8 1-Butene                                               .589    .273
    9 n-Butane                                              1.178    .527
   10 2-Butene                                               .400    .185
   11 2-Butene                                               .273    .127
   12 i-Pentane                                             3.614   1.303
   13 Cyclopentane(?)                                       0.000   0.000
```

14	C5=	.100	.037
15	n-Pentane	.265	.095
16	C5=	.012	.004
17	C5=	.006	.002
18	C5=	.268	.100
19	Dimethyl-Butane	.133	.040
20	2,Methyl-Pentane	1.735	.524
21	n-Hexane	.860	.260
22	C6=	.013	.004
23	3,Methyl-Pentane	.129	.039
24	C6=	.010	.003
25	3-Hexene	.011	.003
26	C6=	.030	.009
27	C6=	.016	.005
28	C6=	.005	.002
29	Methyl-Cyclopentane	.325	.100
30	C6=	.020	.006
31	C6H14	.023	.007
32	Methyl-Cyclopentene	.033	.010
33	Dimethyl-2,Pentene	.004	.001
34	2-Methyl-Hexane	.378	.098
35	3-Methyl-Hexane	.372	.096
36	Dimethyl-Cyclopentane	.083	.022
37	Dimethyl-Cyclopentane	.062	.016
38	Dimethyl-Cyclopentane	.060	.016
39	Methyl-Hexadiene	.025	.007
40	Methyl-Hexadiene	.026	.007
41	n-Heptane	.028	.007
42	Methyl-Hexadiene	.010	.003
43	Methyl-Hexadiene	.023	.006
44	C8H16(branched CycloC5)	.163	.038
45	C7=	.011	.003
46	3,Ethyl-1,Pentene	.079	.021
47	Trimethyl-Cyclopentane	.052	.012
48	Trimethyl-Cyclopentene(?)	.025	.006
49	C8H16(cycloparaf.?)	0.000	0.000
50	Toluene	.827	.233
51	Trimethyl-Cyclopentene(?)	.012	.003
52	Trimethyl-Cyclopentene(?)	.025	.006
53	Methyl-Cyclohexene(?)	.032	.009
54	2,Methyl-Heptane	.058	.013
55	Methyl-Heptane(?)	.067	.015
56	Dimethyl-Cyclohexane(?)	.029	.007
57	2,4 Dimethyl-Hexane	.106	.024
58	Methyl,Ethyl-Cyclopentane	.105	.024
59	Methyl,Ethyl-Cyclopentane	.080	.019
60	Dimethyl-cyclohexane	.032	.007
61	Dimethyl-Cyclohexane	.007	.002
62	Dimethyl-Hexadiene(?)	.073	.017
63	Dimethyl-Cyclohexane	.070	.016
64	n-Octane	.009	.002
65	Dimethyl-Hexadiene(?)	.139	.033
66	Methyl-Heptadiene	.010	.002
67	Ethyl-Hexadiene	.016	.004
68	Dimethyl-Hexadiene(?)	.067	.016
69	Dimethyl-Cyclohexene	.036	.009
70	C8H16(cycloparaf.?)	.097	.023
71	C8H14	.031	.007
72	Dimethyl-Cyclohexene	.012	.003
73	Trimethyl-Cyclohexane	.023	.005

74	Ethyl-Benzene	.099	.024
75	Trimethyl-Cyclohexene	.025	.005
76	p-&m-Xylene	3.577	.876
77	Dimethyl-Heptadiene	.011	.002
78	Trimethyl-Hexane	.059	.012
79	C9H20	.027	.006
80	o-Xylene	.675	.165
81	Trimethyl-Cyclohexane(?)	.049	.010
82	Trimethyl-Cyclohexane(?)	.043	.009
83	Trimethyl-Cyclohexane(?)	.028	.006
84	Trimethyl-Cyclohexene(?)	.012	.003
85	Trimethyl-Cyclohexene(?)	.013	.003
86	Trimethyl-Cyclohexene	.019	.004
87	Dimethyl-Hexadiene	.011	.002
88	C9H16(branched Cyclo-C6= ?)	.008	.002
89	C9H16(branched-cycloC6= ?)	.024	.005
90	i-Propyl-Cyclohexane	.018	.004
91	n-Butyl-Cyclohexane	.020	.004
92	n-Propyl-Benzene	.030	.006
93	C9H16	0.000	0.000
94	Methyl-,Ethyl-Benzene	.349	.076
95	Methyl-,Ethyl-Benzene	.255	.055
96	C9H14(?)	.005	.001
97	n-Nonane	0.000	0.000
98	C8H14(?)	0.000	0.000
99	C8H16(?)	0.000	0.000
100	Trimethyl-Benzene	2.707	.586
101	C10H20(branched-cycloparaf.?)	0.000	0.000
102	C10H20(branched-cycloparaf.?)	0.000	0.000
103	C10H20	.005	.001
104	C10H20(branched-cycloparaf.?)	.004	.001
105	n-Butyl-Cyclohexene(?)	.005	.001
106	Dimethyl-,Ethyl-Benzene	.009	.002
107	C10H20	.005	.001
108	Diethyl-Benzene	.028	.005
109	Propyl-,Methyl-Benzene	.063	.012
110	Propyl-,Methyl-Benzene	.063	.012
111	Tetramethyl-Benzene	.021	.004
112	Dimethyl-,Ethyl-Benzene	.184	.036
113	Tetramethyl-Benzene	2.155	.417
114	Tetramethyl-Benzene	.032	.006
115	C11aromatic	.013	.002
116	C11aromatic	.009	.002
117	C11aromatic	.012	.002
118	C11aromatic	.006	.001
119	C11aromatic	.033	.006
120	Dimethyl-Indane	.041	.007
121	Dimethyl-Indane	.018	.003
122	Dimethyl-Indane	.003	.001
123	C12H18	.008	.001
124	Trimethyl-Indene(?)	.018	.003
125	Dimethyl-Naphtalene	.007	.001
126	C12aromatic	.029	.005
127	none	0.000	0.000
128	none	0.000	0.000
129	none	0.000	0.000
130	none	0.000	0.000
131	Methanol	6.972	5.655
132	Water	53.722	77.462

LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUTIONS

NUMBER	NAME	LIQ HC %	GASEOUS HC %	TOTAL HC %
1	Methane	0.0000	.9682	.5750
2	Ethylene	0.0000	18.7027	11.1078
3	Ethane	0.0000	.2056	.1221
4	Propylene	0.0000	8.5604	5.0841
5	Propane	0.0000	14.1607	8.4102
6	Dimethylether	0.0000	0.0000	0.0000
7	i-Butane	.1497	19.3083	11.5282
8	1-Butene	.0407	2.5571	1.5352
9	n-Butane	.1110	5.0919	3.0692
10	2-Butene	.0529	1.7196	1.0428
11	2-Butene	.0458	1.1666	.7115
12	i-Pentane	2.4377	14.1881	9.4164
13	Cyclopentane(?)	0.0000	0.0000	0.0000
14	C5=	.0947	.3727	.2598
15	n-Pentane	.2729	.9752	.6900
16	C5=	.0764	0.0000	.0310
17	C5=	.0377	0.0000	.0153
18	C5=	.3676	.9266	.6996
19	Dimethyl-Butane	.3024	.3747	.3453
20	2,Methyl-Pentane	4.5903	4.4731	4.5207
21	n-Hexane	2.4662	2.0862	2.2405
22	C6=	.0855	0.0000	.0347
23	3,Methyl-Pentane	.4195	.2785	.3358
24	C6=	.0611	0.0000	.0248
25	3-Hexene	.0682	0.0000	.0277
26	C6=	.1945	0.0000	.0790
27	C6=	.1049	0.0000	.0426
28	C6=	.0336	0.0000	.0136
29	Methyl-Cyclopentane	1.1201	.6593	.8464
30	C6=	.1314	0.0000	.0533
31	C6H14	.1456	0.0000	.0591
32	Methyl-Cyclopentene	.2128	0.0000	.0864
33	Dimethyl-2,Pentene	.0255	0.0000	.0103
34	2-Methyl-Hexane	1.7056	.4902	.9837
35	3-Methyl-Hexane	1.6139	.5276	.9688
36	Dimethyl-Cyclopentane	.5336	0.0000	.2167
37	Dimethyl-Cyclopentane	.3971	0.0000	.1613
38	Dimethyl-Cyclopentane	.3880	0.0000	.1575
39	Methyl-Hexadiene	.1588	0.0000	.0645
40	Methyl-Hexadiene	.1639	0.0000	.0666
41	n-Heptane	.1812	0.0000	.0736
42	Methyl-Hexadiene	.0631	0.0000	.0256
43	Methyl-Hexadiene	.1476	0.0000	.0600
44	C8H16(branched CycloC5)	1.0457	0.0000	.4247
45	C7=	.0682	0.0000	.0277
46	3,Ethyl-1,Pentene	.5051	0.0000	.2051
47	Trimethyl-Cyclopentane	.3360	0.0000	.1365
48	Trimethyl-Cyclopentene(?)	.1578	0.0000	.0641
49	C8H16(cycloparaf.?)	0.0000	0.0000	0.0000
50	Toluene	4.3072	.6846	2.1557
51	Trimethyl-Cyclopentene(?)	.0743	0.0000	.0302
52	Trimethyl-Cyclopentene(?)	.1588	0.0000	.0645
53	Methyl-Cyclohexene(?)	.2026	0.0000	.0823

54	2,Methyl-Heptane	.3737	0.0000	.1518
55	Methyl-Heptane(?)	.4277	0.0000	.1737
56	Dimethyl-Cyclohexane(?)	.1833	0.0000	.0744
57	2,4 Dimethyl-Hexane	.6802	0.0000	.2762
58	Methyl,Ethyl-Cyclopentane	.6720	0.0000	.2729
59	Methyl,Ethyl-Cyclopentane	.5142	0.0000	.2088
60	Dimethyl-cyclohexane	.2057	0.0000	.0835
61	Dimethyl-Cyclohexane	.0479	0.0000	.0194
62	Dimethyl-Hexadiene(?)	.4684	0.0000	.1902
63	Dimethyl-Cyclohexane	.4521	0.0000	.1836
64	n-Octane	.0591	0.0000	.0240
65	Dimethyl-Hexadiene(?)	.8899	0.0000	.3614
66	Methyl-Heptadiene	.0652	0.0000	.0265
67	Ethyl-Hexadiene	.1008	0.0000	.0409
68	Dimethyl-Hexadiene(?)	.4307	0.0000	.1749
69	Dimethyl-Cyclohexene	.2332	0.0000	.0947
70	C8H16(cycloparaf.?)	.6252	0.0000	.2539
71	C8H14	.1965	0.0000	.0798
72	Dimethyl-Cyclohexene	.0743	0.0000	.0302
73	Trimethyl-Cyclohexane	.1466	0.0000	.0595
74	Ethyl-Benzene	.6333	0.0000	.2572
75	Trimethyl-Cyclohexene	.1599	0.0000	.0649
76	p-&m-Xylene	21.1541	1.2304	9.3212
77	Dimethyl-Heptadiene	.0703	0.0000	.0285
78	Trimethyl-Hexane	.3788	0.0000	.1538
79	C9H20	.1751	0.0000	.0711
80	o-Xylene	4.3316	0.0000	1.7590
81	Trimethyl-Cyclohexane(?)	.3116	0.0000	.1265
82	Trimethyl-Cyclohexane(?)	.2780	0.0000	.1129
83	Trimethyl-Cyclohexane(?)	.1802	0.0000	.0732
84	Trimethyl-Cyclohexene(?)	.0784	0.0000	.0318
85	Trimethyl-Cyclohexene(?)	.0866	0.0000	.0351
86	Trimethyl-Cyclohexene	.1202	0.0000	.0488
87	Dimethyl-Hexadiene	.0733	0.0000	.0298
88	C9H16(branched Cyclo-Ce= ?)	.0499	0.0000	.0203
89	C9H16(branched-cycloCe= ?)	.1558	0.0000	.0633
90	i-Propyl-Cyclohexane	.1181	0.0000	.0480
91	n-Butyl-Cyclohexane	.1263	0.0000	.0513
92	n-Propyl-Benzene	.1924	0.0000	.0782
93	C9H16	0.0000	0.0000	0.0000
94	Methyl-,Ethyl-Benzene	2.2422	0.0000	.9105
95	Methyl-,Ethyl-Benzene	1.6353	0.0000	.6641
96	C9H14(?)	.0346	0.0000	.0141
97	n-Nonane	0.0000	0.0000	0.0000
98	C8H14(?)	0.0000	0.0000	0.0000
99	C8H16(?)	0.0000	0.0000	0.0000
100	Trimethyl-Benzene	16.9446	.2917	7.0543
101	C10H20(branched-cycloparaf.?)	0.0000	0.0000	0.0000
102	C10H20(branched-cycloparaf.?)	0.0000	0.0000	0.0000
103	C10H20	.0316	0.0000	.0128
104	C10H20(branched-cycloparaf.?)	.0255	0.0000	.0103
105	n-Butyl-Cyclohexene(?)	.0305	0.0000	.0124
106	Dimethyl-,Ethyl Benzene	.0580	0.0000	.0236
107	C10H20	.0295	0.0000	.0120
108	Diethyl-Benzene	.1772	0.0000	.0719
109	Propyl-,Methyl-Benzene	.4063	0.0000	.1650
110	Propyl-,Methyl-Benzene	.4032	0.0000	.1637
111	Tetramethyl-Benzene	.1324	0.0000	.0538
112	Dimethyl-,Ethyl-Benzene	1.1801	0.0000	.4792
113	Tetramethyl-Benzene	13.8278	0.0000	5.6153

```
 114 Tetramethyl-Benzene               .2067        0.0000        .0839
 115 C11aromatic                       .0815        0.0000        .0331
 116 C11aromatic                       .0601        0.0000        .0244
 117 C11aromatic                       .0764        0.0000        .0310
 118 C11aromatic                       .0397        0.0000        .0161
 119 C11aromatic                       .2087        0.0000        .0848
 120 Dimethyl-Indane                   .2617        0.0000        .1063
 121 Dimethyl-Indane                   .1161        0.0000        .0471
 122 Dimethyl-Indane                   .0183        0.0000        .0074
 123 C12H18                            .0540        0.0000        .0219
 124 Trimethyl-Indene(?)               .1140        0.0000        .0463
 125 Dimethyl-Naphtalene               .0417        0.0000        .0170
 126 C12aromatic                       .1843        0.0000        .0748
 127 none                             0.0000        0.0000       0.0000
 128 none                             0.0000        0.0000       0.0000
 129 none                             0.0000        0.0000       0.0000
 130 none                             0.0000        0.0000       0.0000
 131 Methanol                         0.0000        0.0000       0.0000
 132 Water                            0.0000        0.0000       0.0000


          *****LUMPED LIQUID HYDROCARBON MASS DISTRIBUTION*****

COMPOUND                     WEIGHT % OF LIQUID HYDROCARBONS


C2- Hydrocarbons                           0.00
Propane                                    0.00
Propylene                                  0.00
n-Butane                                    .11
i-Butane                                    .15
Butenes                                     .14
n-Pentane                                   .27
i-Pentane                                  2.44
Pentenes                                    .58
Cyclopentane                               0.00
n-Hexane                                   2.47
Methyl-Pentanes                            5.16
Dimethyl-Butane                             .30
Hexenes                                     .68
Methyl-Cyclopentane                        1.12
Methyl-Cyclopentenes                        .21
n-Heptane                                   .18
C7 branched Paraffins                      3.32
C7 unsaturated chains                      1.13
C7 branched Cycloparaffins                 1.32
C7 branched Cycloolefins                    .20
n-Octane                                    .06
C8 branched Paraffins                      1.48
C8 unsaturated chains                      2.03
C8 branched Cycloparaffins                 4.08
C8 branched Cycloolefins                    .90
n-Nonane                                   0.00
C9 branched Paraffins                       .55
C9 branched Cycloparaffins                 1.03
C9 unsaturated                              .76
C10+ P+O+N                                  .30
Toluene                                    4.31
Ethyl-Benzene                               .63
m-& p-Xylenes                             21.15
```

```
o-Xylene                                          4.33
Trimethyl-Benzenes                               16.94
Methyl-,Ethyl-Benzenes                            3.88
C3-Benzenes                                        .19
Diethyl-Benzenes                                   .18
C3-,Methyl-Benzenes                                .81
Dimethyl-,Ethyl-Benzenes                          1.24
Tetramethyl-Benzenes                             14.17
C11+ Alkyl-Benzenes                                .65
Naphtalenes                                        .55


      *****SUMMARY TABLE OF LIQUID HYDROCARBON COMPOSITION*****

COMPOUND                                WEIGHT % OF LIQUID HYDROCARBONS


C2-C3                                                     0.00
C4 Paraffins                                               .26
C4 Olefins                                                 .14
C5-C9 Paraffins + Cycloparaffins                         23.79
C5-C9 Olefins + Cycloolefins                              6.48
C10+ P+O+N                                                 .30
Toluene                                                   4.31
C8 Aromatics                                             26.12
C9 Aromatics                                             21.01
C10 Aromatics                                            16.39
C11+ Aromatics                                            1.20


        *****LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION*****

COMPOUND                                WEIGHT % OF TOTAL HYDROCARBONS


 Methane                                                   .57
Ethylene                                                 11.11
Ethane                                                     .12
Propylene                                                 5.08
Propane                                                   8.41
i-Butane                                                 11.53
n-Butane                                                  3.07
Butenes                                                   3.29

C5+ HYDROCARBONS

Paraffins + Cycloparaffins                               24.01
Olefins + Cycloolefins                                    3.44
Aromatics                                                28.86
C11+                                                       .51
```

APPENDIX C

CONVERSION OF METHANOL TO GASOLINE:

- parameter estimation for the MTG kinetic rate equation for the model proposed by Chang, using a Marquardt algorithm.
- Listing of program CHANG
- Listing of subroutine BSOLVE

```
FTN7X,L,S
$ema/bill/,/marq/
$cds on
$files 0,3
      PROGRAM CHANG
C**************************************************************************
C  This program calculates the best estimates for the kinetic parameters
C  K1 (b(1)) and K2 (b(2)) to fit the following equation, derived from the
C  model proposed by Chang for the MTG reaction:
C
C            K1 - 2        2*ALPHA*U + BETA - GAMMA     BETA + GAMMA
C    Ln A = -------  Ln ( -------------------------- * --------------)
C            GAMMA         2*ALPHA*U + BETA + GAMMA     BETA - GAMMA
C
C                  K1
C            - (---------) Ln( 1 + BETA*U + ALPHA*U**2 )
C                2*ALPHA
C
C    U = [C2-C5 olefins] / [oxygenates]
C    ALPHA = K1( 1 - K2 )
C    BETA  = K1 - K2 + 2
C    GAMMA = SQRT( BETA**2 - 4*ALPHA )
C
C    This program uses the subroutine BSOLVE , based on the Marquardt algo-
C    rithm, and written by Kuester and Mize ("Optimization techniques with
C    Fortran", Mc Graw-Hill Book Co, p. 240, 1973).
C
C***********************Copyright A. Mahay 1987****************************
      real Wpc(150),Mpc(150),Cov(20,20),Err(20),Bt(30),Tinv(30)
      real Cpc(150) , Corr(30)
      integer Cn(150)
      ema Wpc, Mpc, Cov
      common /marq/ A(25,25),AC(25,25),BMIN(25),BMAX(25)
      real P(200), X(200)
      real B(25), Z(100), Y(100), BV(25)
      integer RR
      real LO,Mfr,Ifr,Mt,Mbo,Mbc,LOc,Meteq,Mtc
      character Rn(20)*5
      character*10 Datafile*16,Rns,Rname
      character*16 Cnum
      Integer ipvt(20)
      EXTERNAL FUNC
      COMMON X
      DATA NO/6/
      Data msize /20/
C
      write(1,*) 'ENTER NUMBER OF RUNS'
      read(1,*) NN
      write(1,*) 'ENTER NUMBER OF DEPENDANT VARIABLES'
      read(1,*) RR
      write(1,*) 'ENTER NUMBER OF PARAMETERS(UNKNOWNS)'
      read(1,*) KK
      write(1,*) 'ENTER NUMBER OF PRODUCT COMPOUNDS'
      read (1,*) Np
C
```

```
      open (20,FILE = 'MTGCNUM.DAT' )
      read(20,*) (Cn(i) , i = 1,Np )
      close (20)
c
      STinv = 0.
      write (NO,590)
 590  format (1x,'RUN#',8X,'C2-C5 OLEF',2X,'C5+ + PARAF')
c
      do 400 i = 1,NN
      write(1,*) 'ENTER # OF THE RUN'
      read(1,'(a5)') Rn(i)
      iend = index(Rn(i),' ')
      Rns = Rn(i)(1:iend-1) // '.DAT'
      Datafile = 'MTG' // Rns
      open (10,FILE=Datafile)
      read (10,*) Np
      read (10,*) (Wpc(j),Mpc(j) , j = 1,Np)
      read (10,*) Cw
      read (10,*) Bt(i),Pr
      read (10,*) Mfr,Ifr
      read (10,*) Mt,T
      read (10,*) Prod
      read (10,*) Mbo,Mbc
      read (10,*) Rt
      close(10)
c
      write (1,*) 'ENTER METOH-DME EQUILIBRIUM CONSTANT '
      read (1,*) X(8*M+i)
      Meteq = sqrt( Mpc(6)*Mpc(132)/X(8*M+i) )
      Bypass = .01 * (Mpc(131) - Meteq ) * Mt / T
      Corr(i) = ( Mfr - Bypass ) / Mfr
      Mtc = .01 * Mt * (100.-Mpc(131) + Meteq )
      Tmfin = (Ifr + Mfr) * Corr(i) / 60.
      Tmfout = Ifr * Corr(i) + Mtc/T
      do j = 1,Np
      Mpc(j) = Mpc(j) * Mt / Mtc
      end do
      Mpc(131) = Meteq * Mt / Mtc
c************************************************************************
c                   Carbon-based product distribution
c************************************************************************
      SCpc = 0.0
      do j = 1,Np
      Cpc(j) = Mpc(j) * Cn(j)
      SCpc = SCpc + Cpc(j)
      end do
      do j = 1,Np
      Cpc(j) = Cpc(j) / SCpc
      end do
c
      LOc= Cpc(2) + Cpc(4) + Cpc(8) + Cpc(10) + Cpc(11) + Cpc(14) +
     $     Cpc(16) + Cpc(17) + Cpc(18)             ! light olefin lump
      Gasoline = 1. - LOc - Cpc(6) - Cpc(131)      ! gasoline lump
C
      X(NN + i) =  Cpc(6) + Cpc(131)               ! oxygenate lump
      X(2*NN + i) =  LOc
      Y(i) =  alog(X(NN+i))
 400  continue
      do i = 1,NN
      X(i) = Bt(i) + 273.15
      end do
c
      write(1,*) 'ENTER INITIAL GUESSES OF PARAMETER VALUES(IN RIGHT OR
     1DER)'
      read (1,*) (B(i) , i =1,KK)
      write (1,*) 'ENTER MINIMUM VALUES OF PARAMETERS'
      read (1,*) (BMIN(i) , i = 1,KK)
      write (1,*) 'ENTER MAXIMUM VALUES OF PARAMETERS'
      read (1,*) (BMAX(i) , i = 1,KK)
C
      FNU = 0.0
      FLA = 0.0
      TAU = 0.0
      EPS = 0.0
      PHMIN = 0.0
      I = 0
      KD = KK
      FV = 0.0
      DO J = 1, KK
          BV(J) = 1
      END DO
      ICON = KK
      ITER = 0
      WRITE (NO,15)
15    FORMAT ( 10X,27HBSOLVE REGRESSION ALGORITHM)
      NN = NN*RR
C
200   CALL BSOLVE(KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,DV,BV,
     $P,FUNC,DERIV,KD,GAMM,Cov)
C
      ITER = ITER + 1
      WRITE (NO,1) ICON, PH, ITER
1     FORMAT (9X,6HICON = , I3, 4X, 5HPH = , E15.8, 4X,
     $16HIteration No. = , I3)
      IF (ICON) 10, 300, 200
10    IF (ICON+1) 20, 60, 200
20    IF (ICON+2) 30, 70, 200
30    IF (ICON+3) 40, 80, 200
40    IF (ICON+4) 50, 90, 200
50    GO TO 95
60    WRITE (NO,4)
4     FORMAT (//, 9X, 32HNo Function Improvement Possible )
      GO TO 300
70    WRITE (NO,5)
5     FORMAT (//,9X, 28HMore Unknowns than Functions)
      GO TO 300
80    WRITE (NO, 6)
6     FORMAT (//,9X, 2HTotal Variables are Zero)
      GO TO 300
90    WRITE (NO,7)
```

```
7       FORMAT (//,9X,79HCorrections Satisfy Convergence Requirements but
       $Lamda Factor (FLA) still Large)
        GO TO 300
95      WRITE (NO,8)
8       FORMAT (//,9X, 20HThis is not Possible)
        GO TO 300
300     WRITE (NO,2)
2       FORMAT (//,9X, 26HSolutions of the Equations)
        DO J = 1, KK
            WRITE(NO,3) J, B(J)
        END DO
3       FORMAT (/,9X, 2HB(, I2, 4H) = , E12.4)
c
c***********************************************************************
c    Inversion of matrix Cov= Transf(Jacobian)*Jacobian
c*********************************************************************
c
        call invrt(Cov,msize,kk,ipvt,ierr)
c
        NN = NN/RR
        write(NO,500)
  500   format(5X,'RUN',3X,'TEMPERATURE (C)',3x,'C% OXYGENAT ',3x,
       1'            metoh + Pdme           ',/)
        write(NO,505)
  505   format(44x,'EXP.',9x,'CALC.',7x,'ERROR%',/)
        do i = 1,NN*RR
        Y(i) = exp( Y(i) )
        Z(i) = exp( Z(i) )
        Err(i) = 100.*(Z(i) - Y(i))/ Y(i)
        end do
        do i = 1,NN
        Rname = 'MTG' // Rn(i)
        write (NO, 510) Rname,Bt(i),X(i+NN),Y(i),Z(i),Err(i)
        end do
        write (NO,501)
  501   format(//,5x,'RUN',3x,'TEMPERATURE (C)',3X,'C2-C5=(CH2 )',3x,
       1'RATE LOLEF PROD.(mole/sec/g cat.)',/)
        write(NO,505)
        do i = 1,NN
        Rname = 'MTG' // Rn(i)
        write (NO, 510) Rname,Bt(i),X(2*NN+i),Y(NN+i),Z(NN+i),Err(NN+i)
        end do
  510   format (3x,a6,8x,f5.2,7x,f7.4,5x,e9.3,5x,e9.3,5x,f4.1)
c
        write(NO,515) Tav
 515    format(/,3x,'1/T AVERAGE=',e9.3,1x,'(1/K)',//)
c
        write(NO,517)
 517    format(5x,3'*','VARIANCE-COVARIANCE MATRIX OF PARAMETER ESTIMATES
       $',3'*',/)
        do i = 1,KK
        write(NO,520) (cov(i,j), j=1,KK)
 520    format(1x,20(e9.2,3x))
        end do
1000    STOP
```

```
      END
C     ******************************************************************
      SUBROUTINE FUNC ( KK, B, NN, Z, FV )
C
      DIMENSION X(200), Z(100), B(25) ,U(100)
      COMMON X
C
      DO JJ = 1, NN
      U(JJ) = X(2*NN+JJ) /  X(NN+JJ)
c     K1   = EXP( B(1) - 1.e3*B(2)/1.987/ X(JJ) )
c     K2   = EXP( B(3) - 1.e3*B(4)/1.987/ X(JJ) )
      ALPHA = B(1) * (1-B(2))
      BETA = B(1)  - B(2)   +2
      GAMMA = SQRT (BETA**2 - 4*ALPHA)
      F1 = (2*ALPHA*U(JJ) + BETA - GAMMA) / (2*ALPHA*U(JJ)+BETA+GAMMA)
      F2 = (BETA+GAMMA) / (BETA-GAMMA)
      F3 = 1 + BETA*U(JJ) + ALPHA*U(JJ)**2
      Z(JJ) =(alog(F1*F2))*((B(1)-2.)/GAMMA)- (alog(F3))*(B(1)/ALPHA/2.)
      END DO
      RETURN
      END
```

```
$ema/bill/,/marq/
$cds on
      SUBROUTINE BSOLVE ( KK, B, NN, Z, Y, PH, FNU, FLA, TAU, EPS,
     $ PHMIN, I, ICON, FV, DV, BV,  P, FUNC, DERIV, KD,
     $ GAMM,Cov)
      Common /marq/ A(25,25),AC(25,25),BMIN(25),BMAX(25)
      dimension Cov(20,20)
      Ema Cov
      DIMENSION  Z(25), Y(25), BV(25),B(25)
      DIMENSION P(150),X(100), FV(25), DV(25)
C
      K = KK
      N= NN
      KP1 = K + 1
      KP2 = KP1 + 1
      KBI1 = K * N
      KBI2 = KBI1 + K
      KZI = KBI2 + K
      IF ( FNU .LE. 0. ) FNU = 10.0
      IF ( FLA .LE. 0. ) FLA = 0.01
      IF ( TAU .LE. 0. ) TAU = 0.001
      IF ( EPS .LE. 0. ) EPS = 0.00002
      IF ( PHMIN .LE. 0. ) PHMIN = 0.
120   KE = 0
130   DO 160 I1 = 1, K
160   IF ( BV(I1) .NE. 0. ) KE = KE + 1
      IF ( KE .GT. 0 ) GO TO 170
162   ICON = - 3
163   GO TO 2120
170   IF ( N .GE. KE ) GO TO 500
180   ICON = -2
190   GO TO 2120
500   I1 = 1
530   IF ( I .GT. 0 ) GO TO 1530
550   DO 560 J1 = 1, K
          J2 = KBI1 + J1
          P(J2) = B(J1)
          J3 = KBI2 + J1
560       P(J3) = ABS ( B(J1) ) + 1.0E-02
      GO TO 1030
590   IF ( PHMIN .GT. PH .AND. I .GT. 1 ) GO TO 625
      DO 620 J1 = 1, K
          N1 = ( J1 - 1 ) * N
          IF ( BV(J1) ) 601, 620, 605
601       CALL DERIV ( K, B, N, Z, P(N1+1), FV, DV, J1, JTEST )
          IF ( JTEST .NE. (-1) ) GO TO 620
          BV(J1) = 1.0
605       DO 606 J2 = 1, K
              J3 = KBI1 + J2
606       P(J3) = B(J2)
          J3 = KBI1 + J1
          J4 = KBI2 + J1
          DEN = 0.001 * AMAX1 ( P(J4), ABS(P(J3)))
          IF ( P(J3) + DEN .LE. BMAX(J1) ) GO TO 55
          P(J3) = P(J3) - DEN
```

```
            DEN = - DEN
            GO TO 56
55          P(J3) = P(J3) + DEN
56          CALL FUNC ( K, P(KBI1+1), N, P(N1+1), FV )
            DO 610 J2 = 1, N
                JB = J2 + N1
610             P(JB) = ( P(JB) - Z(J2) ) / DEN
620     CONTINUE
C
C       SET UP CORRECTION EQUATIONS
C
625     DO 725 J1 = 1, K
            N1 = ( J1 - 1 ) * N
            A(J1,KP1) = 0.
            IF ( BV(J1) ) 630, 692, 630
630         DO 640 J2 = 1, N
                N2 = N1 + J2
640             A(J1,KP1) = A(J1,KP1) + P(N2) * ( Y(J2) - Z(J2) )
650         DO 680 J2 = 1, K
660             A(J1,J2) = 0.
665             N2 = ( J2 - 1 ) * N
670             DO 680 J3 = 1, N
672                 N3 = N1 + J3
674                 N4 = N2 + J3
680         A(J1,J2) = A(J1,J2) + P(N3) * P(N4)
        do 685 jj1 = 1,k
        do 685 jj2 = 1,k
685     Cov(jj1,jj2) = A(jj1,jj2)
            IF ( A(J1,J1) .GT. 1.E-20 ) GO TO 725
692         DO 694 J2 = 1, KP1
694             A(J1,J2) = 0.
695         A(J1,J1) = 1.0
725     CONTINUE
        GN = 0.
        DO 729 J1 = 1, K
729         GN = GN + A(J1,KP1) ** 2
C
C       SCALE CORRECTION EQUATIONS
C
        DO 726 J1 = 1, K
726         A(J1,KP2) = SQRT (A(J1,J1))
        DO 727 J1 = 1, K
            A(J1,KP1) = A(J1,KP1) / A(J1,KP2)
            DO 727 J2 = 1, K
727         A(J1,J2) = A(J1,J2)/ (A(J1,KP2)*A(J2,KP2))
730     FL = FLA / FNU
        GO TO 810
800     FL = FNU * FL
810     DO 840 J1 = 1, K
820         DO 830 J2 = 1, KP1
830             AC(J1,J2) = A(J1,J2)
840         AC(J1,J1) = AC(J1,J1) + FL
C
C       SOLVE CORRECTION EQUATIONS
C
```

```
      DO 930 L1 = 1, K
          L2 = L1 + 1
          DO 910 L3 = L2, KP1
910           AC(L1,L3) = AC(L1,L3) / AC (L1,L1)
          DO 930 L3 = 1,K
          IF (L1-L3) 920, 930, 920
920       DO 925 L4 = L2, KP1
925       AC(L3,L4) = AC(L3,L4) - AC(L1,L4) * AC(L3,L1)
930   CONTINUE
C
      DN = 0.
      DG = 0.
      DO 1028 J1 = 1, K
          AC(J1,KP2) = AC(J1,KP1) / A(J1,KP2)
          J2 = KBI1 + J1
          P(J2) = AMAX1 (BMIN(J1),AMIN1(BMAX(J1),B(J1)+AC(J1,KP2)))
          DG = DG + AC(J1,KP2) * A(J1,KP1) * A(J1,KP2)
          DN = DN + AC(J1,KP2) * AC(J1,KP2)
1028      AC(J1,KP2) = P(J2) - B(J1)
      COSG = DG / SQRT (DN*DG)
      JGAM = 0
      IF (COSG) 1100, 1110, 1110
1100  JGAM = 2
      COSG = - COSG
1110  CONTINUE
      COSG = AMIN1 (COSG, 1.0)
      GAMM = ARCOS(COSG) * 180. / (3.14159265)
      IF ( JGAM .GT. 0 ) GAMM = 180. - GAMM
1030  CALL FUNC (K, P(KBI1+1), N, P(KZI+1), FV)
1500  PHI = 0.
      DO 1520 J1 = 1, N
          J2 = KZI + J1
1520      PHI = PHI + (P(J2)-Y(J1))**2
      IF (PHI .LT. 1.E-20 ) GO TO 3000
      IF ( I .GT. 0 ) GO TO 1540
1521  ICON = K
      GO TO 2110
1540  IF ( PHI .GE. PH ) GO TO 1530
C
C     EPSILON TEST
C
1200  ICON = 0
      DO 1220 J1 = 1, K
          J2 = KBI1 + J1
1220      IF(ABS(AC(J1,KP2))/(TAU+ABS(P(J2))) .GT. EPS) ICON = ICON + 1
      IF ( ICON .EQ. 0 ) GO TO 1400
C
C     GAMMA LAMBDA TEST
C
      IF ( FL .GT. 1.0 .AND. GAMM .GT. 90.0 ) ICON = - 1
      GO TO 2105
C
C     GAMMA EPSILON TEST
C
1400  IF ( FL .GT. 1.0 .AND. GAMM .LE. 45.0 ) ICON = - 4
```

```
      GO TO 2105
C
1530  IF ( I1 - 2 ) 1531, 1531, 2310
1531  I1 = I1 +1
      GO TO (530,590,800), I1
2310  IF ( FL .LT. 1.0E+8 ) GO TO 800
1320  ICON = - 1
C
2105  FLA = FL
      DO 2091 J2 = 1, K
          J3 = KBI1 + J2
2091      B(J2) = P(J3)
2110  DO 2050 J2 = 1, N
          J3 = KZI + J2
2050      Z(J2) = P(J3)
      PH = PHI
      I = I + 1
2120  RETURN
3000  ICON = 0
      GO TO 2105
C
      END
C
C     ********************************************************************
C
      FUNCTION ARCOS(Z)
C
      X = Z
      KEY = 0
      IF ( X .LT. (-1.) ) X= -1.
      IF ( X .GT. 1. ) X = 1.
      IF ( X .GE. (-1.) .AND. X .LT. 0. ) KEY = 1
      IF ( X .LT. 0. ) X = ABS (X)
      IF ( X .EQ. 0. ) GO TO 10
      ARCOS = ATAN (SQRT(1.-X*X) / X )
      IF ( KEY .EQ. 1 ) ARCOS = 3.14159265 - ARCOS
      GO TO 999
10    ARCOS = 1.5707963
999   RETURN
      END
```

APPENDIX D

DIRECT CONVERSION OF SYNGAS TO LIQUID HYDROCARBONS VIA THE METHANOL ROUTE:

- calculation of the conversions, mass balances and weight and molar product distributions.
- Listing of program SGPROD
- Listing of subroutine TCDDAT
- Listing of subroutine TCDPRO
- Printout of the results (for Run SG880519A)

```
ftn 7x,l,s
$files 0,8
$cds on
      PROGRAM SGPROD
C***********************************************************************
C        CALCULATION OF WEIGHT AND MOLAR DISTRIBUTIONS OF THE
C        PRODUCTS FOR THE CONVERSION OF SYNTHETIC GAS TO HYDROCARBONS
C
C  TOTALHC          : file  of  the  cleaned ( corrected  for the extra  and
C   ('TOTHC@.DAT')    missing peaks to match the number of  compounds expec-
C                     ted, N )  weight composition of  the total hydrocarbon
C                     fraction, created from the GC on-line analysis (% peak
C                     area) of  the product stream on the capillary column +
C                     FID.
C  LIQCOMP          : the same as  for TOTALHC , but from the GC analysis of
C   ('LIQ@.DAT')      the liquid hydrocarbon fraction.
C  GASCOMP
C   ('GAS@.DAT')    : the same as  for TOTALHC, but from  the GC analysis of
C                     the non-condensed fraction on the capillary column+FID
C  'SGPRODNAME.DAT': list of the names of  the hydrocarbon compounds of the
C                     product  distribution,  in the order of  appearance in
C                     GC analysis.
C  'SGLUMPNAME.DAT': list of the names of the hydrocarbon lumped species.
C  'SGMOLEWEIGHT.DAT': list  of the  molecular weight of  each  hydrocarbon
C                        compound in  the product distribution,  in the order
C                        of appearance in the GC analysis.
C  'SGCNUM.DAT'     : list of the number of carbons in each hydrocarbon com-
C                     pound, in the order of appearance in the GC analysis.
C  OUTPUTFILE       : file where molar product distribution and  run parame-
C   ('SG@.DAT')       ters are stored, for the kinetic analysis.
C
C   ( @ stands for the id # of the run)
C
C  This program uses subroutine TCDDAT for the creation of files (TCD@.DAT)
C  from the GC on-line analysis of  the product stream with the PORAPAK Q +
C  TCD, and the subroutine TCDPRO for  the calculations from the TCD analy-
C  sis.

C********************* Copyright A. Mahay 1987 *****************************
C
      CHARACTER*1 R1,R0
      CHARACTER*10 RN ,SRN*15
      CHARACTER *16 TOTALHC,LIQCOMP,GASCOMP,OUTPUTFILE
      DIMENSION COPC(10),P(10),T(10),FRIN(10),FNC(10)
      DIMENSION H2(10),CO(10),CH4(10),CO2(10),C2OL(10)
      DIMENSION C2PAR(10),H2O(10),C3OL(10),C3PAR(10),C4(10),C5PLUS(10)
      DIMENSION WLHC(200),WG(200),THC(200),TCD(15),HCM(200)
      DIMENSION SLLHC(20),SC5P(20),C5P(70),TCDMASS(6,15)
      INTEGER PM(200),CN(200), OPTION, LUARY(2), NUMLUS
      REAL LLHC(70),LTHC(15),METOH(10)
      REAL MET,METM,METOHB,MBO,MBC,MBT,LIQM,LIQHCW,LAR,MCAT,NCM
      REAL MBOPC,MBCPC,MBHPC,MBTPC
      CHARACTER NAME(170)*50,LNAME(12)*40,LHCNAME(50)*30,LLNAME(13)*40
      DATA (LNAME(I), I=6,12) /'i-Butane','n-Butane','Butenes',
     $'Paraffins + Cycloparaffins','Olefins + Cycloolefins',
     $'Aromatics','C11+'/
      DATA LLNAME /'C5-C8 Paraffins + Cycloparaffins',
     $'C5-C8 Olefins + Cycloolefins','C9+ P+O+N','Benzene','Toluene',
     $'C8 Aromatics','C9 Aromatics','C10 Aromatics','C11 Aromatics',
     $'C12 Aromatics','C13 Aromatics','C14 Aromatics','C15 Aromatics'/
C***********************************************************************
C
C                                DATA TRANSFER
C
C***********************************************************************
      WRITE( 1,*)'ENTER NUMBER OF COMPOUNDS IN THE HYDROCARBON ANALYSIS'
      READ *,N
      WRITE(1,*)'ENTER RUN TIME(MIN)'
      READ*,TIME
      WRITE(1,*)'ENTER CUMULATIVE TIME ON STREAM(MIN)'
      READ(1,*) CTOS
      WRITE(1,*)'ENTER WEIGHT OF LIQUID HC,WEIGHT OF AQUEOUS FRACTION
     1(GRAMS)'
      READ*,LIQHCW,AF
      WRITE(1,*)'ENTER CORRECTION FACTORS FOR DIMETHYLETHER IN LIQUID
     1HC GC ANALYSIS,IN GASEOUS PRODUCT GC ANALYSIS'
      READ*,CFDMEL,CFDMEG
      WRITE(1,*)'ENTER WT% METOH,AREA% METOH IN CALIBRATION MIXTURE 1,
     1WT% METOH,AREA% METOH IN CALIBRATION MIXTURE 2(GC-TCD ANALYSIS)'
      READ*,WCM1,ACM1,WCM2,ACM2
      WRITE(1,*)'ENTER AREA% OF METHANOL IN AQUEOUS FRACTION
     1(GC-TCD ANALYSIS)'
      READ*,AAF
      WRITE(1,*)'ENTER  RUN IDENTIFICATION'
      WRITE(1,*)'Ex. : for the run #A conducted the 10th of Marsh 1988'
      WRITE(1,*)'       enter 880310A  '
      READ(1,'(A10)') RN
      IEND = INDEX(RN,' ')
      SRN = RN(1:IEND-1) // '.DAT'
      OUTPUTFILE = 'SG' // SRN
      TOTALHC = 'TOTHC' // SRN
      LIQCOMP = 'LIQ' // SRN
      GASCOMP = 'GAS' // SRN
      OPEN(10,FILE='SGMOLEWEIGHT.DAT')
      READ(10,*) (PM(I), I=1,N)
      CLOSE (10)
      write (1,*) 'First file OK !'
      OPEN (20, FILE = 'SGPRODNAME.DAT')
      READ (20,*) (NAME(I), I=1,N)
      CLOSE (20)
      write (1,*) 'Second file OK'
      OPEN (30, FILE = 'SGCNUM.DAT')
      READ (30,*) (CN(I), I=1,N)
      CLOSE (30)
      write(1,*) 'Third file OK !'
      write(1,*) 'Data file for the on-line total hydrocarbon analysis:'
      call Dataread( TOTALHC, THC, N )
      write(1,*) 'Data file for the liquid hydrocarbon analysis:     '
      call Dataread( LIQCOMP, WLHC, N)
      write(1,*) 'Data file for the non-condensed hydrocarbon analysis:'
      call Dataread( GASCOMP, WG, N)
c     OPEN (40, FILE = TOTALHC)
c     READ (40,*) (THC(I), I=1,N)
c     CLOSE (40)
c     write (1,*) 'Fourth file OK !'
c     OPEN (50, FILE = LIQCOMP)
c     READ (50,*) (WLHC(I), I=1,N)
c     CLOSE (50)
c     write (1,*) 'Fith file OK !'
c     OPEN (60, FILE = GASCOMP)
c     READ (60,*) (WG(I), I=1,N)
c     CLOSE (60)
c     write (1,*) 'Sixth file OK !'
      OPEN (65, FILE = 'SGLUMPNAME.DAT')
      READ (65,*) (LHCNAME(I), I=1,50)
      CLOSE (65)
      write (1,*) 'Seventh file OK!'
C*********************************************************************
C          TOTAL, LIQUID ,GAS HYDROCARBON COMPOSITIONS (CORRECTED)
C*********************************************************************
      THC(6) = THC(6)*CFDMET
      WLHC(6) = WLHC(6)*CFDMEL
      WG(6) = WG(6)*CFDMEG
      STHC =  0.
      SWLHC = 0.
      SWG =   0.
      DO 100 I=1,N
      STHC =  STHC + THC(I)
      SWLHC = SWLHC + WLHC(I)
      SWG =   SWG + WG(I)
  100 CONTINUE
      DO 110  I=1,N
      THC(I) =  100*THC(I)/STHC
      WLHC(I) = 100*WLHC(I)/SWLHC
      WG(I) =   100*WG(I)/SWG
  110 CONTINUE
C*********************************************************************
C                         AVERAGE MOLECULAR WEIGHT OF
C          THE GASEOUS LIQUID AND TOTAL HYDROCARBON FRACTIONS
C*********************************************************************
      SMG = 0.
      SML = 0.
      SMT = 0.
      DO 140 I=1,N
      SMG = SMG + WG(I)/PM(I)
      SML = SML + WLHC(I)/PM(I)
      SMT = SMT + THC(I)/PM(I)
  140 CONTINUE
      AMWG = 100/SMG              ! non-condensed hydrocarbon fraction
      AMWL = 100/SML              ! liquid hydrocarbon fraction
      AMWT = 100/SMT              ! total hydrocarbon fraction
C
      Write(1,*) 'Enter output adress for result printing: '
      write(1,*) '    Screen: 1 ; Printer: 6   '
      Read (1,*) NO
```

```
C
C************************************************************************
C         LOCKING THE PRINTER (IO 6) TO AVOID ANY PRINTING INTERFERENCE
C            FROM OTHER USERS WHILE PRINTING THE RESULTS
C************************************************************************
      if ( NO .eq. 6 ) then
          OPTION = 040001B
          LUARY(1) = 6
          NUMLUS = 1
          CALL LURQ (OPTION, LUARY, NUMLUS)
C************************************************************************
          no = 6
          no = 6
          no = 6
      end if
      WRITE (NO,130) RN
  130 FORMAT(1X,18X,40'*',/,1X,18X,'*',38X,'*',/,
     $       1X,18X,'*',5X,'SYNTHESIS GAS CONVERSION RUN',5X,'*',/,
     $       1X,18X,'*',38X,'*',/,
     $       1X,18X,'*',13X,'SG',A8,15X,'*',/,1X,18X,'*',38X,'*',/,
     $       1X,18X,40'*',///)
C***********************************************************************
C          PRELIMINARY CALCULATIONS FROM THE TCD ANALYSIS
C***********************************************************************
C
C<<<<<<<< Data file creation for each hot loop sample analysis >>>>>>>>>
      write(1,*)  'Have you any TCD Analysis file to create or '
      write(1,*)  'to modify ? Answer y or n '
      read(1,*) R0
      IF ( (R0.EQ.'n').OR.(R0.EQ.'N') ) GOTO 125
  120 CALL TCDDAT
      WRITE (1,*) 'MORE TCD GC ANALYSIS ? '
      WRITE (1,*) 'answer y or n '
      READ (1,*) R1
      IF ( (R1.EQ.'y').OR.(R1.EQ.'Y') ) GOTO 120
C<<<<<<<<< Conversions & Product distributions for each analysis >>>>>>>
 125  CALL TCDPRO( RN , COPC , P , T , FRIN , FNC , TCDMASS , MCAT )
      WRITE (1,*) 'GIVE THE 2 TCD ANALYSIS MADE BEFORE AND AFTER FID '
      WRITE (1,*) 'ANALYSIS OF THE HOT LOOP.ENTER ANALYSIS #'
      READ (1,*) K1,K2
      PA = (P(K1) + P(K2))/2
      TA = (T(K1) + T(K2))/2
      FRINA = (FRIN(K1) + FRIN(K2))/2
      FNCA = (FNC(K1) + FNC(K2))/2
      COPCA = (COPC(K1) + COPC(K2))/2
C***********************************************************************
C                TOTAL REACTOR OUTLET MASS DISTRIBUTION
C   Corrected from the TCD analysis for the products non detected
C   by the TCD detector
C***********************************************************************
      STCD = 0.0
      DO i = 1,12
      TCD(i) = ( TCDMASS(k1,i) + TCDMASS(k2,i) )/2
      STCD = STCD + TCD(i)
      ENDDO
      DO i = 1,12
      TCD(i) = 100.*TCD(i) / STCD
      ENDDO
      TCDHC = 0.
      DO I=6,12
      TCDHC = TCDHC + TCD(I)
      ENDDO
      C1COR = 100.*TCD(6)/THC(1) - TCDHC
      C2COR = 100.*(TCD(7) + TCD(8))/(THC(2) + THC(3)) - TCDHC
      C3COR = 100.*(TCD(9) + TCD(10))/(THC(4) + THC(5)) - TCDHC
      WRITE (1,*) 'HC WEIGHT TO BE ADDED TO 100 GRAMS OF PRODUCTS '
      WRITE (1,*) 'DETECTED BY TCD,CALCULATED WITH C1,C2,C3 :'
      WRITE (1,*) C1COR,C2COR,C3COR
      WRITE (1,*) 'ENTER HC CORRECTION MASS FOR TCD ANALYSIS ON '
      WRITE (1,*) 'A 100 GRAMS BASIS OF ALL DETECTED PRODUCTS'
      READ (1,*) CORR
      DO I=1,5
      TCD(I) = TCD(I)/(1+.01*CORR)
      END DO
      HC = (TCDHC +CORR)/(1+.01*CORR)
C***********************************************************************
C        EVALUATION OF THE TOTAL MOLAR FLOW OUT OF THE REACTOR
C        FROM THE FID ANALYSIS OF THE NON CONDENSED FRACTION
C        Hypothesis: No water and methanol is condensed
C***********************************************************************
      Y1 = (WG(1) - THC(1))/WG(1)
      Y2 = (WG(2)+WG(3)-THC(2)-THC(3))/(WG(2)+WG(3))
      Y3 = (WG(4)+WG(5)-THC(4)-THC(5))/(WG(4)+WG(5))
      WRITE(1,*) 'CONDENSED FRACTION OF HC CALCULATED FROM C1,C2 & C3'
      WRITE(1,*) 'FRACTIONS IN TOTAL & NON CONDENSED HC FRACTIONS :'
      WRITE(1,*) Y1,Y2,Y3
      WRITE(1,*) 'ENTER THE FRACTION (.00-1.00) OF CONDENSED HC'
      READ(1,*) Y
      NCM = TCD(1)/2 + TCD(2)/28 + TCD(3)/44 +TCD(4)/18 + TCD(5)/32 +
     $        (1-Y)*HC/AMWG
      TOTM = NCM  - (1-Y)*HC/AMWG + HC/AMWT
C<<<<<<<<<<< Total Molar Flow exiting the reactor(umole/sec) >>>>>>>>>>>>
      FOUT1 = 1E6*FNCA*TOTM/NCM/24200/60
C***********************************************************************
C                           AQUEOUS FRACTION
C***********************************************************************
      WM=WCM1+(WCM2-WCM1)*(AAF-ACM1)/(ACM2-ACM1)
      MET=WM*AF/100
      WAT=AF-MET
C***********************************************************************
C     EVALUATION OF THE TOTAL MOLAR FLOW AT THE EXIT OF THE REACTOR
C                   FROM THE LIQUID ANALYSIS (umole/sec)
C***********************************************************************
      LIQM = LIQHCW/AMWL + WAT/18 + MET/32
      FOUT2 = 1E6*(FNCA/24200 +LIQM/TIME)/60
C***********************************************************************
C                BULK MASS DISTRIBUTION(WT%) OF PRODUCTS
C***********************************************************************
      PROD = 100. - TCD(1) - TCD(2)
      CO2B = 100*TCD(3)/PROD
      H2OB = 100*TCD(4)/PROD
      HCB =  100*HC/PROD
      METOHB = 100*TCD(5)/PROD
C**********************************************************************
C                  MOLAR DISTRIBUTION OF REACTOR OUTLET
C**********************************************************************
      H2M = 100*TCD(1)/2/TOTM
      COM = 100*TCD(2)/28/TOTM
      CO2M = 100*TCD(3)/44/TOTM
      H2OM = 100*TCD(4)/18/TOTM
      METM = 100*TCD(5)/32/TOTM
      DO 180 I=1,N
      HCM(I)=THC(I)*HC/PM(I)/TOTM
  180 CONTINUE
C***********************************************************************
C                          CONVERSIONS
C***********************************************************************
      FIN = 1E6*FRINA/24200/60
      H2CONV = 100*( 1 - H2M*FOUT1/((100-COPCA)*FIN) )
      COCONV = 100*( 1 - COM*FOUT1/(COPCA*FIN) )
C***********************************************************************
C                       MASS BALANCES (ugram/sec)
C***********************************************************************
C
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Oxygen >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
      MBO=( (H2OM + 2*CO2M + METM + COM + HCM(6))*FOUT1
     $                                        - COPCA*FIN )*.16
      MBOPC = 100.*MBO /(.16*COPCA*FIN)
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Carbon >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
      C = 0.
      DO I=1,N
      C = C + CN(I)*HCM(I)
      END DO
      MBC = .12*( (C+COM+CO2M)*FOUT1 - COPCA*FIN )
      MBCPC = 100.*MBC /(.12*COPCA*FIN)
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Hydrogen >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
      MBH = FOUT1*( .02*(H2M + H2OM) + (HC/TOTM -.12*C -.16*HCM(6)) )
     $      -2*(1-.01*COPCA)*FIN
      MBHPC = 100.*MBH /(2*(1-.01*COPCA)*FIN)
C<<<<<<<<<<<<<<<<<< converted mass-mass of products >>>>>>>>>>>>>>>>>>>>
      WCONV = .01*( (1-.01*COPCA)*H2CONV*2 + .01*COPCA*COCONV*28 )*FIN
      WPROD = .01*( CO2M*44 + H2OM*18 + METM*32 + 100*HC/TOTM )*FOUT1
C***********************************************************************
C                         RESULT PRINTING
C***********************************************************************
      OPEN(70,FILE=OUTPUTFILE)
      WRITE(70,*) N,CTOS
      WRITE(70,*) MCAT,TA,PA,COPCA,FIN,FOUT1
      WRITE(70,*) H2M,COM,CO2M,H2OM,METM
      WRITE(70,*) (HCM(I) , I=1,N)
      CLOSE(70)
C
      WRITE(NO,500) RN
  500 FORMAT(/,20X,'PRODUCT DISTRIBUTION OF RUN SG',A8,///)
      WRITE(NO,510) MCAT
  510 FORMAT(1X,'CATALYST WEIGHT=',F7.2,1X,'grams',/)
      WRITE(NO,512) TIME
  512 FORMAT(1X,'TOTAL RUN TIME =',F4.0,1X,'min',/)
      WRITE(NO,515)
  515 FORMAT(1X,'CORRECTION FACTORS FOR THE HYDROCARBON FRACTION NOT
     $DETECTED',/,1X,'IN THE TCD ANALYSIS CALCULATED WITH :'/1X,11X,'C1'
     $,23X,'C2',23X,'C3',/)
      WRITE (NO,516) C1COR,C2COR,C3COR
      WRITE(NO,520)
  520 FORMAT(1X,'FRACTION OF HYDROCARBON CONDENSED CALCULATED FOR THE
     $ESTIMATION OF',/,1X,'THE TOTAL OUTPUT MOLAR FLOW FROM THE MEASURE
     $OF THE FLOW RATE OF NON CONDENSED'/1X,'PRODUCTS ,WITH  THE HYDROCA
     $RBON FRACTION OF :'/1X,11X,'C1',23X,'C2',23X,'C3',/)
      WRITE (NO,516) Y1,Y2,Y3
  516 FORMAT(1X,9X,F5.4,20X,F5.4,20X,F5.4,/)
      FOUT1 = 1E-6*FOUT1*24200*60
      FOUT2 = 1E-6*FOUT2*24200*60
      WRITE(NO,525)
  525 FORMAT(1X,11X,'FLOW RATES AT THE EXIT OF THE REACTOR (ml STP/min)'
     $//1X,2X,'NON CONDENSED',4X,'TOTAL,ESTIMATED FROM FLOW RATE',4X,
     $,'TOTAL,ESTIMATED FROM MASS'/1X,2X,'HYDROCARBONS',11X,
     $'AFTER CONDENSOR',14X,'OF CONDENSED LIQUIDS',/)
      WRITE(NO,526) FNCA,FOUT1,FOUT2
  526 FORMAT(1X,4X,F5.2,20X,F5.2,27X,F5.2,/ )
      WRITE(NO,530)
  530 FORMAT(1X,8X,5'*','AVERAGE MOLECULAR WEIGHT OF HYDROCARBON FRACTIO
     $NS',5'*'//1X,6X,'NON CONDENSED',15X,'LIQUID',20X,'TOTAL',/)
      WRITE(NO,531) AMWG,AMWL,AMWT
  531 FORMAT(1X,9X,F6.2,2(19X,F6.2),/)
      WRITE (NO,540)
  540 FORMAT(1X,25X,5'*','CONVERSIONS (%)',5'*'//1X,18X,'H2',35X,'CO',/)
      WRITE(NO,541) H2CONV,COCONV
  541 FORMAT(1X,16X,F4.1,35X,F4.1,/)
      WRITE(NO,570)
  570 FORMAT(1X,20X,5'*','MASS BALANCES (ugram/sec)',5'*'//
     $1X,3X,'ON OXYGEN',6X,'ON CARBON',5X,'ON HYDROGEN',3X,
     $'CONVERTED MASS',2X,'PRODUCED MASS'/)
      WRITE(NO,572) MBO,MBC,MBH,WCONV,WPROD
      WRITE(NO,573) MBOPC,MBCPC,MBHPC
  572 FORMAT(1X,5X,F5.2,4(11X,F5.2))
  573 FORMAT(1X,5X,F4.1,'%',2(11X,F4.2,'%'),/)
      WRITE(NO,580)
  580 FORMAT(//18X,5'*','BULK PRODUCT MASS DISTRIBUTION(WT%)',5'*',/)
      WRITE(NO,590)
  590 FORMAT(1X,8X,'CO2',16X,'H2O',10X,'HYDROCARBONS',8X,'CH3OH',/)
      WRITE(NO,591) CO2B,H2OB,HCB,METOHB
  591 FORMAT(1X,6X,F6.2,3(12X,F6.2),//)
C
      Write(1,*) 'Enter Output Adress for Product Distributions:'
      Write(1,*) '  Screen :1 ; Printer :6 '
      Read (1,*) NO
      WRITE(NO,640)
C
  640 FORMAT(///,25X,5'*','PRODUCT DISTRIBUTION',5'*',//)
C
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C<<<<< LIQUID,GAS AND TOTAL HYDROCARBON MASS PRODUCT DISTRIBUTIONS >>>>>
      WRITE(NO,671)
  671 FORMAT(//,6X,3'*','LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUT
     $IONS',3'*',//)
      WRITE(NO,672)
  672 FORMAT(1X,'NUMBER',13X,'NAME',12X,'LIQ HC %',2X,'GASEOUS HC %',
     $2X,'TOTAL HC %',//)
      DO I=1,N
      WRITE(NO,674) I,NAME(I),WLHC(I),WG(I),THC(I)
      END DO
  674 FORMAT(1X,I3,1X,A31,1X,F6.3,5X,F6.3,6X,F6.3)
C***********************************************************************
C    LUMPED C5+ TOTAL (C5P) AND LIQUID (LLHC) HYDROCARBON COMPOSITIONS
C***********************************************************************
      LLHC(1)= WLHC(15)
      C5P(1) = THC(15)
      LLHC(2)= WLHC(12)
      C5P(2) = THC(12)
      LLHC(3)= WLHC(14)+WLHC(16)+WLHC(17)+WLHC(18)
      C5P(3) = THC(14) +THC(16) +THC(17) +THC(18)
      LLHC(4)= WLHC(13)
      C5P(4) = THC(13)
      LLHC(5)= WLHC(24)
      C5P(5) = THC(24)
      LLHC(6)= WLHC(19)+WLHC(21)+WLHC(22)
      C5P(6) = THC(19) +THC(21) +THC(22)
      LLHC(7)= WLHC(20)
      C5P(7) = THC(20)
      LLHC(8)= WLHC(23)+WLHC(31)
      C5P(8) = THC(23) +THC(31)
      DO I=25,29
      LLHC(8)= LLHC(8)+WLHC(I)
      C5P(8) = C5P(8) +THC(I)
      END DO
      LLHC(9)= WLHC(34)
      C5P(9) = THC(34)
      LLHC(10)= WLHC(30)
      C5P(10) = THC(30)
      LLHC(11)= WLHC(32)
      C5P(11) = THC(32)
      LLHC(12)= 0.
      C5P(12) = 0.
      LLHC(13)= WLHC(35)+WLHC(36)
      C5P(13) = THC(35) +THC(36)
      LLHC(14)= 0.
      C5P(14) = 0.
      LLHC(15)= WLHC(37)+WLHC(38)+WLHC(39)+WLHC(41)+WLHC(42)
      C5P(15) = THC(37) +THC(38) +THC(39) +THC(41) +THC(42)
      LLHC(16)= WLHC(40)
      C5P(16) = THC(40)
      LLHC(17)= 0.
      C5P(17) = 0.
      LLHC(18)= WLHC(44)+WLHC(56)
      C5P(18) = THC(44) +THC(56)
      LLHC(19)= WLHC(49)+WLHC(50)+WLHC(51)
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 C5P(19) = THC(49) +THC(50) +THC(51)
 LLHC(20)= WLHC(43)+WLHC(45)+WLHC(46)+WLHC(52)+WLHC(53)+WLHC(54)+
$          WLHC(55)+WLHC(57)+WLHC(58)+WLHC(59)+WLHC(60)+WLHC(61)+
$          WLHC(63)+WLHC(64)+WLHC(65)
 C5P(20) = THC(43)+THC(45)+THC(46)+THC(52)+THC(53)+THC(54)+THC(55)
$ +THC(57)+THC(58)+THC(59)+THC(60)+THC(61)+THC(63)+THC(64)+THC(65)
 LLHC(21)= WLHC(47)+WLHC(62)+WLHC(66)+WLHC(67)+WLHC(68)
 C5P(21) = THC(47) +THC(62) +THC(66) +THC(67) +THC(68)
 LLHC(22)= WLHC(71)+WLHC(73)+WLHC(74)+WLHC(75)+WLHC(76)+WLHC(83)
 C5P(22) = THC(71) +THC(73) +THC(74) +THC(75) +THC(76) +THC(83)
 LLHC(23)= WLHC(33)
 C5P(23) = THC(33)
 LLHC(24)= WLHC(48)
 C5P(24) = THC(48)
 LLHC(25)= WLHC(69)
 C5P(25) = THC(69)
 LLHC(26)= WLHC(70)
 C5P(26) = THC(70)
 LLHC(27)= WLHC(72)
 C5P(27) = THC(72)
 LLHC(28)= WLHC(80)+WLHC(82)+WLHC(84)
 C5P(28) = THC(80) +THC(82) +THC(84)
 LLHC(29)= WLHC(78)+WLHC(79)+WLHC(81)
 C5P(29) = THC(78) +THC(79) +THC(81)
 LLHC(30)= WLHC(77)
 C5P(30) = THC(77)
 LLHC(31)= WLHC(87)+WLHC(89)
 C5P(31) = THC(87) +THC(89)
 LLHC(32)= WLHC(88)+WLHC(91)
 C5P(32) = THC(88) +THC(91)
 LLHC(33)= WLHC(90)+WLHC(92)+WLHC(94)+WLHC(95)+WLHC(96)
 C5P(33) = THC(90) +THC(92) +THC(94) +THC(95) +THC(96)
 LLHC(34)= WLHC(97)+WLHC(98)+WLHC(101)
 C5P(34) = THC(97) +THC(98) +THC(101)
 LLHC(35)= WLHC(85)
 C5P(35) = THC(85)
 LLHC(36)= WLHC(86)
 C5P(36) = THC(86)
 LLHC(37)= WLHC(93)+WLHC(99)+WLHC(100)
 C5P(37) = THC(93) +THC(99) +THC(100)
 LLHC(38)= WLHC(102)
 C5P(38) = THC(102)
 LLHC(39)= WLHC(103)+WLHC(104)+WLHC(105)+WLHC(109)+WLHC(110)+
$          WLHC(111)+WLHC(113)+WLHC(119)
 C5P(39) = THC(103) +THC(104) +THC(105) +THC(109) +THC(110) +
$          THC(111) +THC(113) +THC(119)
 LLHC(40)= WLHC(106)+WLHC(107)+WLHC(108)+WLHC(116)+WLHC(117)+
$          WLHC(118)
 C5P(40) = THC(106) +THC(107) +THC(108) +THC(116) +THC(117) +
$          THC(118)
 LLHC(41)= WLHC(120)+WLHC(121)
 C5P(41) = THC(120) +THC(121)
 LLHC(42)= WLHC(125)+WLHC(132)
 C5P(42) = THC(125) +THC(132)
 LLHC(43)= WLHC(123)
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      C5P(43) = THC(123)
      LLHC(44)= WLHC(112)+WLHC(114)+WLHC(115)+WLHC(122)+WLHC(127)
      C5P(44) = THC(112) +THC(114) +THC(115) +THC(122) +THC(127)
      LLHC(45)= WLHC(128)+WLHC(129)+WLHC(130)
      C5P(45) = THC(128) +THC(129) +THC(130)
      LLHC(46)= WLHC(126)
      C5P(46) = THC(126)
      LLHC(47)= WLHC(124)+WLHC(133)
      C5P(47) = THC(124) +THC(133)
      LLHC(48)= WLHC(134)
      C5P(48) = THC(134)
      DO I=135,141
      LLHC(48)= LLHC(48)+WLHC(I)
      C5P(48) = C5P(48) +THC(I)
      END DO
      LLHC(49)= WLHC(142)
      C5P(49) = THC(142)
      DO I=143,149
      LLHC(49)= LLHC(49)+WLHC(I)
      C5P(49) = C5P(49) +THC(I)
      END DO
      LLHC(50)= WLHC(150)
      C5P(50) = THC(150)
      DO I=151,159
      LLHC(50)= LLHC(50)+WLHC(I)
      C5P(50) = C5P(50) +THC(I)
      END DO
C ************** C4- total & liquid hydrocarbon fractions*************
      WLHC4M = WLHC(1)
      THC4M = THC(1)
      DO I=2,11
      WLHC4M = WLHC4M + WLHC(I)
      THC4M = THC4M + THC(I)
      END DO
C***** Normalization C5+ total and liquid hydrocarbon distribution*****
      DO I=1,50
      LLHC(I)= 100*LLHC(I)/(100-WLHC4M)
      C5P(I) = 100*C5P(I)/(100-THC4M)
      END DO
C
C******SUMMARY OF C5+TOTAL & LIQUID HYDROCARBON LUMPED COMPOSITION********
C
      SLLHC(2)= LLHC(3)+LLHC(8)+LLHC(11)+LLHC(14)+LLHC(16)+LLHC(19)+
     $          LLHC(21)
      SC5P(2) = C5P(3) +C5P(8) +C5P(11) +C5P(14) +C5P(16) +C5P(19) +
     $          C5P(21)
      SLLHC(1)= -SLLHC(2)
      SC5P(1) = -SC5P(2)
      DO I=1,21
      SLLHC(1)= SLLHC(1) + LLHC(I)
      SC5P(1) = SC5P(1) + C5P(I)
      END DO
      SLLHC(3)= LLHC(22)
      SC5P(3) = C5P(22)
      SLLHC(4)= LLHC(23)
      SC5P(4) = C5P(23)
      SLLHC(5)= LLHC(24)
      SC5P(5) = C5P(24)
      SLLHC(6)= LLHC(25)+LLHC(26)+LLHC(27)
      SC5P(6) = C5P(25) +C5P(26) +C5P(27)
      SLLHC(7)= LLHC(28)+LLHC(29)+LLHC(30)+LLHC(35)+LLHC(36)
      SC5P(7) = C5P(28) +C5P(29) +C5P(30) +C5P(35) +C5P(36)
      SLLHC(8)= LLHC(31)+LLHC(32)+LLHC(33)+LLHC(34)+LLHC(37)+LLHC(38)
      SC5P(8) = C5P(31) +C5P(32) +C5P(33) +C5P(34) +C5P(37) +C5P(38)
      SLLHC(9)= LLHC(39)+LLHC(40)+LLHC(41)
      SC5P(9) = C5P(39) +C5P(40) +C5P(41)
      SLLHC(10)= LLHC(42)+LLHC(43)+LLHC(44)+LLHC(45)
      SC5P(10) = C5P(42) +C5P(43) +C5P(44) +C5P(45)
      SLLHC(11)= LLHC(46)+LLHC(47)+LLHC(48)
      SC5P(11) = C5P(46) +C5P(47) +C5P(48)
      SLLHC(12)= LLHC(49)
      SC5P(12) = C5P(49)
      SLLHC(13)= LLHC(50)
      SC5P(13) = C5P(50)
      LAR=0
      DO I=4,13
      LAR=LAR+SLLHC(I)
      END DO
C
C***************LUMPED TOTAL HYDROCARBON DISTRIBUTION********************
C
      DO I=1,5
      LTHC(I) = THC(I)
      END DO
      LTHC(6) = THC(7)
      LTHC(7) = THC(9)
      LTHC(8) = THC(8) + THC(10) + THC(11)
      LTHC(9) = SC5P(1) + SC5P(3)
      LTHC(10) = SC5P(2)
      LTHC(11) = SC5P(4)+SC5P(5)+SC5P(6)+SC5P(7)+SC5P(8)
      LTHC(12) = SC5P(9)+SC5P(10)+SC5P(11)+SC5P(12)+SC5P(13)
      DO I=9,12
      LTHC(I) = LTHC(I)*(1-.01*THC4M)
      END DO
C
C*******************PRINTING OF TABLES OF LUMPED DISTRIBUTIONS***********
C
      write(1,*) 'Enter output adress for result printing: '
      write(1,*) '   Screen: 1, HP Printer: 6, PANASONIC Printer: 47 '
      read(1,*) NO
      WRITE(NO,680)
  680 FORMAT('1',1x,4X,5'*','LUMPED, LIQUID & TOTAL C5+ HYDROCARBON MASS
     $ DISTRIBUTIONS',5'*',/)
      WRITE(NO,682)
  682 FORMAT(1X,'COMPOUND',31X,'LIQUID',14X,'TOTAL',//)
      DO I=1,50
      WRITE(NO,684) LHCNAME(I),LLHC(I),C5P(I)
      END DO
  684 FORMAT(1X,A30,7X,F6.2,13X,F6.2)
C
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      WRITE(NO,690)
  690 FORMAT('1',1x,2X,5'*','SUMMARY TABLE OF LIQUID & TOTAL C5+ HYDROCA
     $RBON COMPOSITIONS',5'*',/)
      WRITE(NO,692)
  692 FORMAT(1X,3x,,'COMPOUND',35X,'LIQUID',11X,'TOTAL',//)
      DO I=1,13
      WRITE(NO,694) LLNAME(I),SLLHC(I),SC5P(I)
      END DO
  694 FORMAT(1X,3x,A40,1X,F7.2,10X,F7.2)
C
      WRITE(NO,700)
  700 FORMAT(//,10X,5'*','LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION',
     $5'*',/)
      WRITE(NO,702)
  702 FORMAT(1X,3x,'COMPOUND',28X,'WEIGHT % OF TOTAL HYDROCARBONS',//)
      DO I=1,5
      WRITE(NO,710) NAME(I),LTHC(I)
      ENDDO
      DO I=6,8
      WRITE(NO,710) LNAME(I),LTHC(I)
      END DO
      WRITE(NO,704)
  704 FORMAT(/,1X,3x,'C5+ HYDROCARBONS',/)
      DO I=9,12
      WRITE(NO,710) LNAME(I),LTHC(I)
      END DO
  710 FORMAT(1X,3x,A40,9X,F7.2)
      WRITE (NO,720)
  720 FORMAT('1')
C
C*****SUMMARY TABLE FOR THE RUN (OPERATING CONDITIONS AND RESULTS)*******
C
      write(1,*) 'Enter output adress for result printing:'
      write(1,*) '  Screen: 1 ; HP Printer: 6 ; PANASONIC Printer: 47'
      read(1,*) NO
      WRITE (NO,130) RN
C
      WRITE(NO,730)
  730 FORMAT(5X,28'*',/,1X,8X,'OPERATING CONDITIONS',/,1X,4X,28'*',/)
      WRITE(NO,740) TA
  740 FORMAT(22X,'TEMPERATURE: ',f5.1,1X,'oC')
      Patm= 1.+ PA/14.7
      WRITE(NO,745) Patm
  745 FORMAT(25X,'PRESSURE: ',F5.1,1X,'atm')
      RH2CO = (100.-COPCA)/COPCA
      WRITE(NO,750) RH2CO
  750 FORMAT(22X,'H2/CO ratio: ',F4.2)
      WRITE(NO,755) FIN
      FIN = 1E-6*FIN*24200*60
  755 FORMAT(19X,'FEED FLOW RATE: ',F5.1,1X,'mlSTP/min')
      WHSV = 60*FIN/MCAT
      WRITE(NO,760) WHSV
  760 FORMAT(29X,'WHSV: ',F4.0,1X,'mlSTP/gcat/hr')
      WRITE(NO,765) TIME
  765 FORMAT(20X,'TEST DURATION: ',F4.0,1X,'minutes')
```

```
      WRITE(NO,770) CTOS
  770 FORMAT(8X,'CUMULATIVE TIME ON STREAM: ',F4.0,1X,'minutes',/)
      WRITE(NO,775)
  775 FORMAT(5X,20'*',/,1X,8X,'CONVERSIONS',/,1X,4X,20'*',/)
      WRITE(NO,780) COCONV
  780 FORMAT(7X,'CO CONVERSION: ',F4.1,1X,'%')
      WRITE(NO,785) H2CONV
  785 FORMAT(7X,'H2 CONVERSION: ',F4.1,1X,'%',/)
      WRITE(NO,790)
  790 FORMAT(5X,39'*',/,1X,8X,'PRODUCT MASS DISTRIBUTION (WT%)',/,
     $       1X,4X,39'*',/)
      WRITE(NO,795) CO2B
  795 FORMAT(18X,'CO2      ',F5.2)
      WRITE(NO,800) H2OB
  800 FORMAT(18X,'H2O      ',F5.2)
      WRITE(NO,805) HCB
  805 FORMAT(18X,'HC       ',F5.2)
      WRITE(NO,810) METOHB
  810 FORMAT(18X,'METOH    ',F5.2,/)
      WRITE(NO,815)
  815 FORMAT(5X,23'*',/,1X,9X,'MASS BALANCE',/,1X,4X,23'*',//,
     $       24X,'OUT - IN (ugram/sec)',4X,'%ERROR',/)
      WRITE(NO,820) MBC,MBCPC
  820 FORMAT(12X,'CARBON:',13X,F7.1,10X,F4.1)
      WRITE(NO,825) MBH,MBHPC
  825 FORMAT(10X,'HYDROGEN:',13X,F7.1,10X,F4.1)
      WRITE(NO,830) MBO,MBOPC
  830 FORMAT(12X,'OXYGEN:',13X,F7.1,10X,F4.1,/)
      MBT = MBC + MBO + MBH
      MBTPC = (MBC + MBO + MBH)/(MBC/MBCPC + MBO/MBOPC + MBH/MBHPH)
      WRITE(NO,835) MBT,MBTPC
  835 FORMAT(13X,'TOTAL:',13X,F7.1,10X,F4.1,/,'1')
C
C*********************************************************************
C                         UNLOCKING THE PRINTER
C*********************************************************************
      OPTION = 140000B
      CALL LURQ (OPTION, LUARY, NUMLUS)
C
      STOP
      END
C*********************************************************************
c                          SUBROUTINE DATAREAD
c    This subroutine read the data files where GC analysis of the products
c  were stored . Those files may have been typed in manually, or may have
c  been created via RS-232 data transfer from the integrator. In the last
c  case, the transferred file has been decoded (programs CONV92 or CONV93)
c  then cleaned (program CLEAN).
C*********************************************************************
      subroutine DATAREAD( DATAFILE, VECTOR, N)
      character*16 DATAFILE, R*1
      dimension VECTOR(200)
      integer Area
c
      open (40, FILE = DATAFILE )
      write(1,*) 'This file was typed in manually? Answer y or n .'
      read(1,*) R
      if ( ( R.eq.'y').or.( R.eq.'Y') ) then
         read (40,*) ( VECTOR(I), I = 1,N)
         write(1,*) '!!!!!! file read !!!!!! '
      else
         do i=1,N
         read(40,800) Ipeak, Time, Area, VECTOR(I)
         enddo
         write(1,*) '!!!!!!!! file read !!!!!!!!'
      endif
      close(40)
  800 format(i3,2x,f7.2,2x,i10,2x,f7.3)
c
      return
      end
```

```
ftn7x,l,s
$files 0,1
$cds on
      subroutine tcddat (RN)
c*************************************************************************
c   This program  stores  in a file  TCD'id#'.DAT  run conditions and  peak
c   area of  the TCD analysis of  the content of  the hot  GC 1ml injection
c   loop on the PORAPAK Q packed column.
c   When  the peaks are  identified through  the subroutine TIMEMATCH,  the
c   bracketting  times  for  each  peak  correspond  to an analysis  with a
c   PORAPAK column  1/8" o.d., 6ft long   with a 30 ml/min He carrier flow-
c   rate, and the following temperature program :
c           -10oC (1min) --(40oC/min)--> 240oC (15 min)
c   In this case,  the program  reads  the peak area  from  a raw  datafile
c   TCDREP'id#'.DAT.
c   The times are presently set for the analysis of  the products of syngas
c   conversion in the following order: H2, CO, CH4, CO2, C2=, C2, H2O, C3=,
c   C3, CH3OH, C4's, C5+.  It is advised  to check the time matching  which
c   may drift  with the column aging or  slight changes in  analysis condi-
c   tions.
c
c************************ Copyright 1988 A. Mahay ************************
c
      real MFC,LEAK,METOH
      character*20 OUTPUTFILE,TCDFILE*20,RN*10,SRN*15,R1*1,In*81,Cut*11
      character K*1
      common Length
c
c Data input
c
      write(1,*)'Enter Analysis Identification'
      write(1,*) ' Ex. : for analysis #1 for the run #A conducted '
      write(1,*) '       the 10th of March 1988, enter 1 '
      read (1,*) K
      iend = index(rn,' ')
      srn = rn(1:iend-1) // '*' // K // '.dat'
      outputfile = 'tcd' // srn
      open (10,file = outputfile)
c
      write(1,*) 'Enter in the same order:'
      write(1,*)
      write(1,*) '- Run time(min)(TIME),H2/CO ratio,CO mole%(COPC)'
      write(1,*)
      write(1,*) '- Pressure(psig)(P),Bed Temperature(oC)(T)'
      write(1,*) '  MFC indication (MFC)'
      write(1,*)
      write(1,*) '- Flow in (FRIN),Flow out (FNC) (ml STP/min)'
      write(1,*) '  Correction for leaks (ml STP/min): LEAK '
      write(1,*)
      write(1,*) '- Loop temperatures for bypass and reactor '
      write(1,*) '  injections (oC) ( TLOOPBYP AND TLOOP )'
      write(1,*)
      write(1,*) '- Correction factors for pressure drop for bypass and'
      write(1,*) '  reactor loop injections : PCORBYP , PCOR '
      write(1,*)
      write(1,*) '- H2 and CO peak area for bypass injection :'
      write(1,*) '  H2BYP AND COBYP '
c
      read (1,*) TIME, SYNGAS, COPC, P, T, MFC, FRIN, FNC, LEAK,
     $           TLOOPBYP, TLOOP, PCORBYP, PCOR, H2BYP, COBYP
c
      write(1,*)
      write(1,*) 'Was the TCD analysis report transferred to HP1000 '
      write(1,*) ' via RS-232 ?'
      read (1,*) R1
      if ( (R1.eq.'N').or.(R1.eq.'n') ) then

          write(1,*) '- Enter in this order Peak area for H2, CO, CH4,'
          write(1,*) '  CO2, C2OL, C2PAR, H2O, C3OL, C3PAR, CH3OH, C4s,'
          write(1,*) '  C5+'
          read (1,*) H2,CO,CH4,CO2,C2OL,C2PAR,H2O,C3OL,C3PAR,METOH,C4,
     $               C5PLUS
      else
          TCDFILE = 'tcdrep' // srn
          open (20, file = TCDFILE )
c
c   Selection of the Integrator
c
      write(1,*) 'Indicate on which integrator the report was produced:'
      write(1,*) ' Enter,  for 3392A : 1  ;   for 3393A : 2  '
      read (1,*) INT
      if ( INT.eq.1 ) then
         Assign 100 to Label
         IS = 2
      else
         Assign 200 to Label
         IS = 1
      endif
c
c           Find the length of the file ( number of record from the top
c           of the report to the last peak record) and reset the file to
c           first peak record.
c
          Mark = 0
    3     read (20,'(A42)') In
          Mark = Mark + 1
          Cut = In(IS:10+IS)
          If ( Cut.ne.' TOTAL AREA' ) goto 3
          rewind 20
          Length = Mark - 1
c
          do 5, i = 1,4
             read (20,'(A81)') In
    5     continue
          Mark = 4
c
          call TIMEMATCH ( .42, .50, Area, Ptime, INT, Mark )
          H2 = Area
          call TIMEMATCH ( .65, .80, Area, Ptime, INT, Mark )
          CO = Area
         call TIMEMATCH ( .65, .80, Area, Ptime, INT, Mark )
         if ( Area.ne.0) CO = Area
         call TIMEMATCH (1.50,1.70, Area, Ptime, INT, Mark )
         CH4 = Area
         call TIMEMATCH (2.85,3.10, Area, Ptime, INT, Mark )
         CO2 = Area
         call TIMEMATCH (3.65,3.85, Area, Ptime, INT, Mark )
         C2OL = Area
         call TIMEMATCH (3.95,4.20, Area, Ptime, INT, Mark )
         C2PAR = Area
         call TIMEMATCH (4.45,4.80, Area, Ptime, INT, Mark )
         H2O = Area
         call TIMEMATCH (5.25,5.60, Area, Ptime, INT, Mark )
         C3OL = Area
         call TIMEMATCH (5.30,5.75, Area, Ptime, INT, Mark )
         C3PAR = Area
         METOH = 0.
         C4 = 0.
         if ( Mark.eq.Length) goto 15
   10    call TIMEMATCH (6.30,6.80, Area, Ptime, INT, Mark )
         C4 = C4 + Area
         if ( Mark.eq.Length) goto 15
         if ( Ptime.le.6.80 ) goto 10
   15    C5PLUS = 0
         if ( Mark.eq.length) goto 20
         do i = mark+1, Length
            read (20, FMT = Label) Ptime, Area, PC
            C5PLUS = C5PLUS + Area
         enddo
   20    close(20)
      endif
c
      write(10,*) TIME ,SYNGAS ,COPC ,P ,T ,MFC ,FRIN ,
     $            FNC ,LEAK ,H2BYP ,H2 ,TLOOPBYP ,
     $            TLOOP ,PCORBYP ,PCOR ,COBYP ,CO ,
     $            CH4 ,CO2 ,C2OL ,C2PAR ,H2O ,C3OL ,C3PAR ,
     $            METOH ,C4 ,C5PLUS
      close(10)
c
  100 format ( 3x, f6.2, 1x, f10.0, 17x, f7.3 )
  200 format ( 3x, f6.2, 1x, f10.0, 13x, f7.3 )
 1000 return
      end
c***********************************************************************
c   TIMEMATCH is a subroutine used for matching the GC peaks from the
c   reports transferred via RS-232 from the integrator. The meanings of
c   the arguments are:
c     - T1 and T2 : GC retention times between which the peak is expected
c                   to appear,
c     - Area : Peak area,
c     - Ptime : retention time of the peak,
c     - INT : integrator number for the selection of the reading format;
c     - Mark : Record number corresponding to the peak, in the report file.
c***********************************************************************
c
```

```
      Subroutine TIMEMATCH ( T1,T2, Area, Ptime, INT, Mark)
      Common  Length
      if (INT.eq.1) then
         Assign 100 to Label
      else
         Assign 200 to Label
      endif
      If (Mark.eq.Length) then
         Area = 0.
         Goto 130
      Else
      Endif
 120  Read (20,FMT = Label)  Ptime, Area, PC
      If ( Ptime.GT.T2) then
          Area = 0.
          Backspace 20
          Goto 130
      Else
          Mark = Mark+1
          Endif
      If ( (Ptime.GE.T1).and.(Ptime.LE.T2) ) goto 130
      If ( Mark.eq.Length) then
         Area = 0.
         goto 130
      Else
      goto 120
      Endif
  100 format(3x, f6.2, 1x, f10.0, 17x, f7.3)
  200 format(3x, f6.2, 1x, f10.0, 13x, f7.3)
  130 return
      end
```

```
ftn7x,l,s
$files 0,1
$cds on
      subroutine tcdpro (RN, COPC ,P ,T ,FRIN ,FNC ,TCDMASS ,MCAT)
c***********************************************************************
c   This program  calculates  CO and H2  conversions,  product distribution
c   (CO2,H2O,Hydrocarbons and oxygenates)  and mass balances  from the  TCD
c   analysis  of  the content of  the  hot  1ml GC injection loop  with the
c   PORAPAK Q packed column.
c   This program  uses datafiles  TCD@.DAT  ( @ stands for  the run  and GC
c   on-line analysis id # ), created with  the program TCDDAT, where injec-
c   tion parameters and peak area are stored.
c
c*********************** Copyright 1988 A. Mahay ***************************
c
      dimension TCDMASS(6,15)
      dimension TIME(10),SYNGAS(10),COF(10),COPC(10),P(10),T(10)
      dimension FRIN(10),FNC(10),H2BYP(10),H2(10),TLOOPBYP(10),TLOOP(10)
      dimension PCORBYP(10),PCOR(10);COBYP(10),CO(10),CH4(10),CO2(10)
      dimension C2OL(10),C2PAR(10),H2O(10),C3OL(10),C3PAR(10),C4(10)
      dimension C5PLUS(10),FLOW(10),H2CONV(10),COCONV(10),HC(10)
      dimension VLOOPBYP(10),VLOOP(10)
      real MFC(10),LEAK(10),METOH(10),MASSCONV(10),PROD(10)
      real MCAT
      character*1 R,R1
      character*20 DATAFILE
      character NUM*3, SNUM*6, RN*10, SRN*7
      character*80 COMMENT1,COMMENT2
C     data (name(i) ,i=1,10) /'CO2','H2O','CH4','C2=','C2','C3=','C3',
C    $                         'C4s','C5+','METOH'/
c Data input
c
      write(1,*) 'A maximum of  6 GC analysis can be entered'
c
      write(1,*)
      write(1,*) 'Enter the mass of catalyst (grams)'
      read(1,*) MCAT
c
c   Comments
c
      write(1,*) 'Enter catalyst designation and preteatment (complete'
      write(1,*) ' the comment line to 80 characters with blanks)'
      read(1,'(A80)') COMMENT1
      write(1,*) 'More comments ? (y or n)'
      read(1,'(A1)') R1
      if ( R1 .eq. 'n') goto 110
      write(1,*) 'Enter your extra comment line'
      read(1,'(A80)') COMMENT2
c
 110  i = 0
 100  i = i+1
c
      write(1,*) 'Enter datafile number.'
      write(1,*) '  Ex. : for analysis #1 in the run#A of '
      write(1,*) '         Sep. the 10th 1987, enter 1   '
      read(1,'(A3)') NUM
      IEND = index(NUM,' ')
      SNUM = NUM(1:IEND-1) // '.DAT '
      IEND = index(RN,' ')
      SRN = RN(1:IEND-1)
      DATAFILE = 'TCD' // SRN // '*' // SNUM
c
      open (10,file = DATAFILE)
      read(10,*) TIME(i),SYNGAS(i),COF(i),P(i),T(i),MFC(i),FRIN(i),
     $           FNC(i),LEAK(i),H2BYP(i),H2(i),TLOOPBYP(i),
     $           TLOOP(i),PCORBYP(i),PCOR(i),COBYP(i),CO(i),
     $           CH4(i),CO2(i),C2OL(i),C2PAR(i),H2O(i),C3OL(i),C3PAR(i),
     $           METOH(i),C4(i),C5PLUS(i)
      close(10)
      write(1,*) ' !!!!Datafile read !!!! '
c
      FLOW(i) = FRIN(i)/24/MCAT
      TLOOPBYP(i) = TLOOPBYP(i) + 273.
      TLOOP(i) = TLOOP(i) + 273.
      FNC(i) = FNC(i) + LEAK(i)
      FACT = FNC(i)*TLOOP(i)*PCORBYP(i)/(FRIN(i)*TLOOPBYP(i)*PCOR(i))
c
      H2(i) = H2CAL( H2(i) )
      H2BYP(i) = H2CAL( H2BYP(i) )
      CO(i) = COCAL( CO(i) )
      COBYP(i) = COCAL( COBYP(i) )
c
      COPC(i) = 100.*COBYP(i)/(COBYP(i) + H2BYP(i))
      H2CONV(i) = 100.*(1.- H2(i) * FACT / H2BYP(i))
      COCONV(i) = 100.*(1.- CO(i) * FACT / COBYP(i))
c *************************************************************************
c   Calculation of the mass of each component contained in the GC loop from
c   the GC peak area, using calibration curves.
c   The  factor F0  is introduced  to take into account  small  variations,
c   between different injections, of the loop temperature and pressure drop
c   (mainly affected by the gas flowrate through the loop,  at a given tem-
c   perature),  which affect  the amount  of the loop content injected.  The
c   factor which takes into account the pressure drop, PCOR,  is determined
c   in function of  the non-condensed gas flowrate  measured ( provided the
c   contribution of  the condensed  fraction to  the total gas flowrate  of
c   the stream exiting the reactor can be neglected ), using a pre-establi-
c   shed curve.
c *************************************************************************
      F0 = TLOOP(i)/295./PCOR(i)
      TCDMASS(i,1) = 2*H2(i)*F0 / 24.2
      TCDMASS(i,2) = 28*CO(i)*F0 / 24.2
      TCDMASS(i,3) = CO2(i)*F0 / 1200.
      TCDMASS(i,4) = ( .6E-3*H2O(i) - .6 )*F0
      TCDMASS(i,5) = METOH(i)*F0 / 1580.
      TCDMASS(i,6) = CH4(i)*F0 / 2080.
      TCDMASS(i,7) = C2OL(i)*F0 / 1800.
      TCDMASS(i,8) = C2PAR(i)*F0 / 1800.
      TCDMASS(i,9) = C3OL(i)*F0 /1538.
      TCDMASS(i,10)= C3PAR(i)*F0 / 1615.
      TCDMASS(i,11)= C4(i)*F0 / 1666.
      TCDMASS(i,12)= C5PLUS(i)*F0 / 1600.
c *************************************************************************
c  Estimation of the loop volume from its content, for each analysis, in-
c  cluding the bypass injection.
c**************************************************************************
      VLOOPBYP(i) = (H2BYP(i) + COBYP(i))*TLOOPBYP(i)/295./PCORBYP(i)
      VLOOP(i) = TCDMASS(i,1)/2    + TCDMASS(i,2)/28  + TCDMASS(I,3)/44 +
     $           TCDMASS(i,4)/18   + TCDMASS(i,5)/32  + TCDMASS(i,6)/16 +
     $           TCDMASS(i,7)/28   + TCDMASS(i,8)/30  + TCDMASS(i,9)/42 +
     $           TCDMASS(i,10)/44 + TCDMASS(i,11)/58 + TCDMASS(i,12)/80
      VLOOP(i) = VLOOP(i)*24.2
c**************************************************************************
c           Calculation of total mass product distribution
c**************************************************************************
      PROD(i) = 0.0
      DO j = 3,12
      PROD(i) = PROD(i) + TCDMASS(i,j)
      ENDDO
c
      H2O(i) = 100.*TCDMASS(i,4) / PROD(i)
      CO2(i) = 100.*TCDMASS(i,3) / PROD(i)
      HC(i)  = 100. - H2O(i) - CO2(i)
c**************************************************************************
c          Calculation of Hydrocarbon mass product distribution
c**************************************************************************
      F1 = 1.E4  / (PROD(i)*HC(i))
      CH4(i)    = TCDMASS(i,6)  * F1
      C2OL(i)   = TCDMASS(i,7)  * F1
      C2PAR(i)  = TCDMASS(i,8)  * F1
      C3OL(i)   = TCDMASS(i,9)  * F1
      C3PAR(i)  = TCDMASS(i,10) * F1
      METOH(i)  = TCDMASS(i,5)  * F1
      C4(i)     = TCDMASS(i,11) * F1
      C5PLUS(i) = TCDMASS(i,12) * F1
c**************************************************************************
c  Calculation of the converted mass (MASSCONV) and the product mass (PROD)
c *************************************************************************
      PROD(i) = PROD(i) * FNC(i) / 1000.
      MASSCONV(i) = FRIN(i) * (.01*COPC(i)*28.*COCONV(i) +
     $                        (1.-.01*COPC(i))*2.*H2CONV(i) )/2420.
c
      if (i-6) 150,200,200
 150  write(1,*) 'do you want to enter another GC loop analysis(y or n)'
      read(1,* ) R
      if ( R .EQ. 'y') goto 100
c
 200  write(1,*) 'Enter output adress for printing the results :'
      write(1,*) '     Screen : 1 ; Printer : 6 '
      read (1,*) NO
      write(NO,40) COMMENT1
      if ( R1 .eq. 'n' ) goto 210
      write(NO,50) COMMENT2
 210  write(NO,60)
  60  format(1x,24x,5'*','TCD ANALYSIS RESULTS',5'*',//,79('-'))
      write(NO,10)' TIME (min)         ', (TIME(j) ,j=1,i)
      write(NO,10)' H2/CO             ', (SYNGAS(j) , j=1,i)
      write(NO,10)' P (psig)          ', (P(j) , j=1,i)
      write(NO,10)' T (oC)            ', (T(j) , j=1,i)
      write(NO,10)' MFC setpoint      ', (MFC(j) , j=1,i)
      write(NO,10)' FLOW(mmole/gr.cat)',(FLOW(j) , j=1,i)
      write(NO,30)
      write(NO,10)' CO conv (%)       ', (COCONV(j) , j=1,i)
      write(NO,10)' H2 conv (%)       ', (H2CONV(j) , j=1,i)
      write(NO,30)
      write(NO,15)
 15   format(1X,'Product mass distribution',/)
      write(NO,10)'    CO2            ', (CO2(j) , j=1,i)
      write(NO,10)'    H2O            ', (H2O(j) , j=1,i)
      write(NO,10)' Hydroc.+Oxygenates', (HC(j) , j=1,i)
      write(NO,30)
      write(NO,20)
 20   format(1X,'Hydrocarbons(+Oxygenates) mass distribution',/)
      write(NO,10)'   CH4             ', (CH4(j) , j=1,i)
      write(NO,10)'   C2=             ', (C2OL(j) , j=1,i)
      write(NO,10)'   C2              ', (C2PAR(j) , j=1,i)
      write(NO,10)'   C3=             ', (C3OL(j) , j=1,i)
      write(NO,10)'   C3              ', (C3PAR(j) , j=1,i)
      write(NO,10)'   C4s             ', (C4(j) , j=1,i)
      write(NO,10)'   C5+             ', (C5PLUS(j) , j=1,i)
      write(NO,10)'   METOH           ', (METOH(j) ,  j=1,i)
      write(NO,30)
      write(NO,25)
 25   format(1X,'Mass Balance',/)
      write(NO,10)' CO+H2conv.(mg/min)', (MASSCONV(j) , j=1,i)
      write(NO,10)' Prod. mass(mg/min)', (PROD(j) , j=1,i)
      write(NO,10)' Loop vol. bypa(ul)', (VLOOPBYP(j) , j=1,i)
      write(NO,10)' Loop vol.     (ul)', (VLOOP(j) , j=1,i)
      write(NO,10)' CO feed    (mole%)', (COPC(j) , j=1,i)
      write(NO,30)
 50   format(3X,A80,//)
 40   format(///,3X,A80)
 30   format(1X,79('-'))
 10   format (1X,A19,6(F10.1))
      return
      end
c
c****************************************************************************
c    Calibration function to compute H2 volume (ul) from the TCD peak area
c        Calibration Date : Jan. 88
c        Valid for the Area range (Range set at 2^0 on HP5890A) :
c          3300 (100 ulSTP) to 122000 (1000 ulSTP)
c****************************************************************************
c
      FUNCTION H2CAL(X)
      H2CAL = 63.184 + .01217628*X - 8.75560127512E-08 * X**2
     $                             + 6.67971183518E-13 * X**3
     $                             - 2.05991445345E-18 * X**4
      return
      end
c****************************************************************************
```

```
c    Calibration Function  to compute CO volume (ul) from the TCD peak area
c        Calibration Date : Jan. 88
c        Valid for the Area Range (Range set at 2^0 on HP5890A) :
c         88000 (50 ulSTP) to 1.65E+6 (1000 ulSTP)
c*****************************************************************************
c
      FUNCTION COCAL(X)
      COCAL = -7.821 + .000630125*X - 1.79924571963E-10 * X**2
     $                              + 2.12702430797E-16 * X**3
     $                              - 6.14736379050E-23 * X**4
      return
      end
```

Appendix E

DIRECT CONVERSION OF SYNGAS TO LIQUID HYDROCARBONS VIA THE METHANOL ROUTE:

- kinetic parameter estimation for the methanol synthesis rate equation, using a Marquardt algorithm.
- Listing of program SGKIN

```
         ****************************************
         *                                      *
         *     SYNTHESIS GAS CONVERSION RUN     *
         *                                      *
         *              SG880519A               *
         *                                      *
         ****************************************


****************************
   OPERATING CONDITIONS
****************************

                 TEMPERATURE: 375.0 oC
                    PRESSURE:  42.5 atm
                 H2/CO ratio: 1.15
              FEED FLOW RATE: 154.3
                        WHSV: 860. mlSTP/gcat/hr
               TEST DURATION: 227. minutes
    CUMULATIVE TIME ON STREAM: 150. minutes

********************
   CONVERSIONS
********************

  CO CONVERSION: 34.2 %
  H2 CONVERSION: 18.0 %

***************************************
   PRODUCT MASS DISTRIBUTION (WT%)
***************************************

             CO2      73.67
             H2O       2.23
             HC       24.10
             METOH     0.00

***********************
    MASS BALANCE
***********************

                    OUT - IN (ugram/sec)    %ERROR

       CARBON:                33.0           3.8
     HYDROGEN:                -4.0          -2.4
       OXYGEN:                48.9           4.3

        TOTAL:                78.0           3.2
```

```
*****SUMMARY TABLE OF LIQUID & TOTAL C5+ HYDROCARBON COMPOSITIONS*****

COMPOUND                                        LIQUID          TOTAL


C5-C8 Paraffins + Cycloparaffins                  .40            4.52
C5-C8 Olefins + Cycloolefins                      .00             .07
C9+ P+O+N                                        0.00            0.00
Benzene                                           .04             .42
Toluene                                          1.27            2.90
C8 Aromatics                                    18.24           18.63
C9 Aromatics                                    42.63           36.77
C10 Aromatics                                   16.88           15.98
C11 Aromatics                                   10.25            8.56
C12 Aromatics                                    7.40            8.24
C13 Aromatics                                    2.38            3.28
C14 Aromatics                                     .39             .51
C15 Aromatics                                     .07             .11


      *****LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION*****

COMPOUND                              WEIGHT % OF TOTAL HYDROCARBONS


Methane                                            3.41
Ethylene                                            .27
Ethane                                             3.80
Propylene                                           .16
Propane                                           15.26
i-Butane                                           2.29
n-Butane                                           2.30
Butenes                                             .10

C5+ HYDROCARBONS

Paraffins + Cycloparaffins                         3.27
Olefins + Cycloolefins                              .05
Aromatics                                         54.09
C11+                                              14.99
```

```
                 ***************************************
                 *                                     *
                 *      SYNTHESIS GAS CONVERSION RUN   *
                 *                                     *
                 *             SG880519A               *
                 *                                     *
                 ***************************************



  Cat.: 63% Zn/Cr*25/75*calc350C, 27% H-ZSM5 (MZ-2), 10% Versal950 (Al203 Binder)
  Pret.: Calc.350oC*2hrs, 7.8%H2 in He*1atm*150ml/min*250C^300oC*16hrs, ^375oC^He


                         *****TCD ANALYSIS RESULTS*****

 -----------------------------------------------------------------------------
  TIME (min)                 25.0       53.0      213.0
  H2/CO                       1.0        1.0        1.0
  P (psig)                  605.0      610.0      610.0
  T (oC)                    375.0      375.0      375.0
  MFC setpoint               10.0       10.0       10.0
  FLOW(mmole/gr.cat)           .6         .6         .6
 -----------------------------------------------------------------------------
  CO conv (%)                35.7       32.6       32.3
  H2 conv (%)                18.9       16.1       16.1
 -----------------------------------------------------------------------------
 Product mass distribution

     CO2                     89.1       89.3       88.5
     H2O                      3.7        2.7        3.2
  Hydroc.+Oxygenates          7.2        8.0        8.3
 -----------------------------------------------------------------------------
 Hydrocarbons(+Oxygenates) mass distribution

    CH4                      12.5       14.0       14.1
    C2=                       0.0        0.0        2.7
    C2                       12.4       14.3       16.2
    C3=                       0.0        0.0        0.0
    C3                       60.2       57.2       48.9
    C4s                       7.3        7.0       13.2
    C5+                       7.6        7.4        4.9
    METOH                     0.0        0.0        0.0
 -----------------------------------------------------------------------------
 Mass Balance

  CO+H2conv.(mg/min)         45.0       41.0       41.8
  Prod. mass(mg/min)         39.5       40.1       36.0
  Loop vol. bypa(ul)        995.6      995.6     1009.2
  Loop vol.      (ul)      1025.3     1017.7     1020.1
  CO feed     (mole%)        46.6       46.6       47.4
 -----------------------------------------------------------------------------

                    PRODUCT DISTRIBUTION OF RUN SG880519A
```

```
CATALYST WEIGHT=  15.63 grams

TOTAL RUN TIME =227. min

CORRECTION FACTORS FOR THE HYDROCARBON FRACTION NOT    DETECTED
IN THE TCD ANALYSIS CALCULATED WITH :
          C1                             C2                             C3

        7.697                          6.166                          6.684

FRACTION OF HYDROCARBON CONDENSED CALCULATED FOR THE   ESTIMATION OF
THE TOTAL OUTPUT MOLAR FLOW FROM THE MEASURE OF THE FLOW RATE OF NON CONDENSED
PRODUCTS ,WITH  THE HYDROCARBON FRACTION OF :
          C1                             C2                             C3

        .6282                          .6180                          .5874

             FLOW RATES AT THE EXIT OF THE REACTOR (ml STP/min)

  NON CONDENSED    TOTAL,ESTIMATED FROM FLOW RATE    TOTAL,ESTIMATED FROM MASS
  HYDROCARBONS            AFTER CONDENSOR             OF CONDENSED LIQUIDS

    190.0                      191.4                          190.7

          *****AVERAGE MOLECULAR WEIGHT OF HYDROCARBON FRACTIONS*****

      NON CONDENSED                  LIQUID                       TOTAL

          43.95                      123.97                       72.38

                             *****CONVERSIONS (%)*****

                  H2                                     CO

                 18.0                                   34.2

                     *****MASS BALANCES (ugram/sec)*****

     ON OXYGEN      ON CARBON      ON HYDROGEN    CONVERTED MASS  PRODUCED MASS

       48.92          33.05          -4.00          717.4            795.3
        4.3%           3.83%         -2.4%


                 *****BULK PRODUCT MASS DISTRIBUTION(WT%)*****

         CO2              H2O          HYDROCARBONS        CH3OH

        73.67             2.23           24.10              0.00
```

*****LUMPED, LIQUID & TOTAL C5+ HYDROCARBON MASS DISTRIBUTIONS*****

COMPOUND	LIQUID	TOTAL
n-Pentane	.00	.42
i-Pentane	.01	1.99
Pentenes	0.00	.07
Cyclopentane	0.00	0.00
n-Hexane	.00	.05
Methyl-Pentanes	.01	.45
Dimethyl-Butane	.00	.17
Hexenes	0.00	0.00
Cyclohexane	.01	.04
Methyl-Cyclopentane	.01	.18
Methyl-Cyclopentenes	0.00	0.00
n-Heptane	0.00	0.00
C7 branched Paraffins	.01	0.00
C7 unsaturated chains	0.00	0.00
C7 branched Cycloparaffins	.10	.52
C7 branched Cycloolefins	0.00	0.00
n-Octane	0.00	0.00
C8 branched Paraffins	.02	.04
C8 unsaturated chains	0.00	0.00
C8 branched Cycloparaffins	.22	.66
C8 branched Cycloolefins	.00	0.00
C9+ P+O+N	0.00	0.00
Benzene	.04	.42
Toluene	1.27	2.90
Ethyl-Benzene	.20	.25
m-& p-Xylenes	13.76	14.21
o-Xylene	4.28	4.17
Trimethyl-Benzenes	41.13	35.39
Methyl-,Ethyl-Benzenes	1.33	1.24
C3-Benzenes	.01	0.00
Diethyl-Benzenes	.05	0.00
C3-,Methyl-Benzenes	.04	0.00
Dimethyl-,Ethyl-Benzenes	1.76	1.59
Tetramethyl-Benzenes	13.16	12.76
Indane	.15	.14
Indene	.01	0.00
Methyl-Indane	1.80	1.57
Tetralin	.07	.06
C11 alkyl-Benzenes	1.95	1.80
Dimethyl-Indanes	3.89	3.05
Methyl-Naphtalene	4.41	3.72
C12 alkyl-Benzenes	.17	.07
C12 alkyl-Indanes	.08	0.00
C12 alkyl-Tetralins	.99	.91
C12 alkyl-Naphtalenes	6.15	7.26
C13 alkyl-Indanes	.08	.06
C13 alkyl-Tetralins	.18	.10
C13 alkyl-Naphtalenes	2.13	3.12
C14 alkyl-Naphtalenes	.39	.51
C15 alkyl-Naphtalenes	.07	.11

```
                    *****PRODUCT DISTRIBUTION*****


     ***LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUTIONS***

NUMBER              NAME              LIQ HC %  GASEOUS HC %  TOTAL HC %


   1 Methane                            0.000      9.159        3.405
   2 Ethylene                           0.000      0.000         .273
   3 Ethane                             0.000     10.668        3.802
   4 Propylene                          0.000      0.000         .164
   5 Propane                             .002     37.382       15.261
   6 Dimethylether                      0.000      0.000        0.000
   7 i-Butane                            .002      5.430        2.286
   8 1-Butene                           0.000       .087         .049
   9 n-Butane                            .003      5.283        2.305
  10 2-Butene                           0.000      0.000         .029
  11 2-Butene                           0.000      0.000         .020
  12 i-Pentane                           .012      3.404        1.440
  13 Cyclopentane(?)                    0.000      0.000        0.000
  14 C5=                                0.000      0.000        0.000
  15 n-Pentane                           .004       .567         .305
  16 C5=                                0.000      0.000        0.000
  17 C5=                                0.000       .075         .026
  18 C5=                                0.000      0.000         .028
  19 Unknown                             .002       .083         .040
  20 Dimethyl-Butane                     .004       .288         .125
  21 2,Methyl-Pentane                    .004       .265         .116
  22 3,Methyl-Pentane                    .009       .370         .169
  23 C6=                                0.000      0.000        0.000
  24 n-Hexane                            .002      0.000         .037
  25 C6=                                0.000      0.000        0.000
  26 C6=                                0.000      0.000        0.000
  27 C6=                                0.000      0.000        0.000
  28 C6=                                0.000      0.000        0.000
  29 C6=                                0.000      0.000        0.000
  30 Methyl-Cyclopentane                 .012       .286         .128
  31 4-Methyl,1-Pentene(?)              0.000      0.000        0.000
  32 Unknown                            0.000      0.000        0.000
  33 Benzene                             .039       .351         .306
  34 Cyclohexane                         .007       .149         .032
  35 2,3-Dimethyl-Pentane                .004       .061        0.000
  36 3-Methyl-Hexane                     .002      0.000        0.000
  37 Dimethyl-Cyclopentane               .009       .088         .049
  38 Dimethyl-Cyclopentane               .009       .079         .044
  39 Dimethyl-Cyclopentane               .007       .068         .041
  40 Dimethyl-Cyclopentene              0.000      0.000        0.000
  41 Unknown                            0.000      0.000        0.000
  42 Methyl-Cyclohexane                  .074       .471         .239
  43 1,1,3-Trimethyl-Cyclopentane        .006      0.000        0.000
  44 4-Methyl-Heptane(?)                 .010       .090         .029
  45 1,2,4-Trimethyl-Cyclopentane        .009       .052        0.000
```

46	1,2,3-Trimethyl-Cyclopentane	0.000	0.000	0.000
47	C8 Cycloolefin(?)	.002	0.000	0.000
48	Toluene	1.268	2.472	2.099
49	C8=(?)	0.000	0.000	0.000
50	C8=(?)	0.000	0.000	0.000
51	C8=(?)	0.000	0.000	0.000
52	Trimethyl-Cyclopentane	.005	0.000	0.000
53	Dimethyl-Cyclohexane	.044	.105	.069
54	Dimethyl-Cyclohexane	.030	.074	.046
55	Dimethyl-Cyclohexane	.003	0.000	0.000
56	2,4 Dimethyl-Hexane	.010	0.000	0.000
57	Methyl,Ethyl-Cyclopentane	.016	0.000	0.000
58	Methyl,Ethyl-Cyclopentane	0.000	0.000	0.000
59	Dimethyl-Cyclohexane	.010	0.000	0.000
60	Dimethyl-Cyclohexane	.041	.095	.060
61	Dimethyl-Cyclohexane	.006	0.000	0.000
62	C8 Cycloolefin(?)	0.000	0.000	0.000
63	Methyl-,Ethyl-Cyclopentane	.006	0.000	0.000
64	Dimethyl-Cyclohexane	.006	0.000	0.000
65	Ethyl-Cyclohexane	.035	.144	.302
66	C8 Cycloolefin(?)	.001	0.000	0.000
67	C8 Cycloolefin(?)	.002	0.000	0.000
68	C8 Cycloolefin(?)	0.000	0.000	0.000
69	Ethyl-Benzene	.198	.080	.182
70	p- & m-Xylenes	13.758	7.961	10.289
71	Unknown	0.000	0.000	0.000
72	o-Xylene	4.279	2.078	3.016
73	Unknown	0.000	0.000	0.000
74	Unknown	0.000	0.000	0.000
75	Unknown	0.000	0.000	0.000
76	Unknown	0.000	0.000	0.000
77	Propyl-Benzene	.009	0.000	0.000
78	Methyl-,Ethyl-Benzene	.782	.195	.532
79	Methyl-,Ethyl-Benzene	.376	0.000	.246
80	Trimethyl-Benzene	7.176	1.641	4.361
81	Methyl-,Ethyl-Benzene	.175	0.000	.117
82	Trimethyl-Benzene	31.256	6.549	19.512
83	Unknown	0.000	0.000	0.000
84	Trimethyl-Benzene	2.691	.523	1.752
85	Indane	.152	0.000	.103
86	Indene	.013	0.000	0.000
87	Diethyl-Benzene	0.000	0.000	0.000
88	Methyl-,Propyl-Benzene	.027	0.000	0.000
89	Diethyl-Benzene	.053	0.000	0.000
90	Dimethyl-,Ethyl-Benzene	.560	.117	.364
91	Methyl,-Propyl-Benzene	.009	0.000	0.000
92	Dimethyl-,Ethyl-Benzene	.272	0.000	.176
93	Methyl-Indane	.371	0.000	.240
94	Dimethyl-,Ethyl-Benzene	.815	.128	.543
95	Dimethyl-,Ethyl-Benzene	.018	0.000	0.000
96	Dimethyl-,Ethyl-Benzene	.091	0.000	.064
97	Tetramethyl-Benzene	6.574	1.307	4.592
98	Tetramethyl-Benzene	5.257	.983	3.703
99	Methyl-Indane	1.002	.084	.652
100	Methyl-Indane	.426	0.000	.244
101	Tetramethyl-Benzene	1.329	.226	.946
102	Tetraline	.073	0.000	.047
103	Dimethyl-,n-Propyl-Benzene	.040	0.000	.079
104	Dimethyl-,n-Propyl-Benzene	.040	0.000	.034
105	Dimethyl-,n-Propyl-Benzene	.431	0.000	.316

106	Dimethyl-Indane	.330	0.000	0.000
107	Dimethyl-Indane	.700	.072	.219
108	Dimethyl-Indane	.097	0.000	.451
109	Trimethyl-,Ethyl-Benzene	.301	.084	.304
110	Trimethyl-,Ethyl-Benzene	.094	0.000	.047
111	Dimethyl-,Isopropyl-Benzene	.070	0.000	0.000
112	Dimethyl-Tetralin	.060	0.000	.036
113	Dimethyl-,Isopropyl-Benzene(?)	.071	0.000	.045
114	Dimethyl-Tetralin	.101	0.000	.066
115	Dimethyl-Tetralin	.078	0.000	.042
116	Dimethyl-Indane	1.244	.018	.617
117	Dimethyl-Indane	1.488	0.000	.366
118	Dimethyl-Indane	.036	.055	.551
119	Pentamethyl-Benzene	.902	.210	.475
120	Methyl-Naphtalene	3.386	0.000	1.957
121	Methyl-Naphtalene	1.025	0.000	.738
122	Dimethyl-Tetralin	.255	0.000	.183
123	Trimethyl-Indane	.082	0.000	0.000
124	Trimethyl-Tetralin	.141	.044	.071
125	Trimethyl-,Isopropyl-Benzene	.101	0.000	0.000
126	Tetramethyl-Indane	.079	0.000	.043
127	Dimethyl-Tetralin	.499	0.000	.335
128	Dimethyl-Naphtalene	2.989	0.000	2.601
129	Dimethyl-Naphtalene	2.696	0.000	2.253
130	Dimethyl-Naphtalene	.467	0.000	.403
131	C12H30	.045	0.000	0.000
132	Hexamethyl-Benzene	.070	0.000	.048
133	Trimethyl-Tetralin	.035	0.000	0.000
134	Isopropyl-Naphtalene	.060	0.000	.038
135	Isopropyl-Naphtalene	.482	0.000	.452
136	Trimethyl-Naphtalene	.413	0.000	0.000
137	Trimethyl-Naphtalene	.372	0.000	.836
138	Trimethyl-Naphtalene	.236	0.000	0.000
139	Trimethyl-Naphtalene	.300	0.000	.646
140	Trimethyl-Naphtalene	.255	0.000	.288
141	Trimethyl-Naphtalene	.011	0.000	0.000
142	Methyl-,Propyl-Naphtalene	.025	0.000	0.000
143	Methyl-,Isopropyl-Naphtalene	.069	0.000	.115
144	Methyl-,Isopropyl-Naphtalene	.016	0.000	0.000
145	Methyl-,Isopropyl-Naphtalene	.064	0.000	.094
146	Methyl-,Isopropyl-Naphtalene	.032	0.000	0.000
147	Methyl-,Propyl-Naphtalene	.072	0.000	0.000
148	Methyl-,Propyl-Naphtalene	.054	0.000	.083
149	Methyl-,Propyl-Naphtalene	.061	0.000	.075
150	C15H18 Naphtalene	.022	0.000	0.000
151	C15H18 Naphtalene	.028	0.000	0.000
152	C15H18 Naphtalene	0.000	0.000	0.000
153	C15h18 Naphtalene	0.000	0.000	0.000
154	C15h18 Naphtalene	.022	0.000	.080
155	Dimethyi-,Isopropyl-Naphtalene	0.000	0.000	0.000
156	Dimethyl-,Isopropyl-Naphtalene	0.000	0.000	0.000
157	Dimethyl-,Isopropyl-Naphtalene	0.000	0.000	0.000
158	Dimethyl-,Isopropyl-Naphtalene	0.000	0.000	0.000
159	Dimethyl-,Isopropyl-Naphtalene	0.000	0.000	0.000

```
FTN7X,L,S
$ema/bill/
$cds on
$files 0,3
C*************************************************************************
c      The present version treats only the Methanol Synthesis reaction
c      the methanol conversion to hydrocarbons being complete and the
c      water gas shift reaction being at equilibrium.
c      the rate of the methanol synthesis has the following form:
c
c                  PH2**2 * PCO - (PCH3OH/PH2**2/PCO/KMS)
c    r = --------------------------------------------------- * EXP(B(5)*t)
c          B(1)**3 * ( 1 + B(2)*PH2 + B(3)*PCO + B(4)*PCO2 )**3
c
c      where,
c        - PH2,PCO,PCO2,PCH3OH are the fugacities  (atm)
c        - KMS is the thermodynamic equlibrium constant for the methanol
c          synthesis reaction
c        - t is the cumulative time on stream (min)
c
C*********************** Copyright 1988 A. Mahay ******************************
c
      PROGRAM SGKIN
      real HCm(200),Cov(20,20),Err(100),Bt(50),Tinv(50)
      real Corr(30)
      character*7 Rns
      ema  HCm, Cov
      common /marq/ A(25,25),AC(25,25),BMIN(25),BMAX(25)
      real P(400), X(350), Mcat ,METm ,BETA(50),KWGS(50),KPWGS(50)
      real B(25), Z(100), Y(100), BV(25)
      integer RR ,OPTION, LUARY(2), NUMLUS
      real LO
      character*15 Datafile*16,Rn,Rname
      character*7 Rid(45)
      Integer ipvt(20)
      EXTERNAL FUNC ,CFUG
      COMMON X ,BETA ,Pra ,KWGS,KPWGS, Tav
      Write(1,*) 'Enter adress for the printing of the results;'
      Write(1,*) ' SCREEN: 1 ; HP PRINTER : 6 ; PANASONIC PRINTER : 47'
      Read (1,*) NO
C*************************************************************************
C   LOCKING THE PRINTER (io 6) TO AVOID ANY PRINTING INTERFERENCE FROM
C   OTHER USERS
C*************************************************************************
      if ( NO.eq.6 ) then
          option = 040001B
          luary(1) = 6
          numlus = 1
          call lurq (option,luary,numlus)
      no = 6
      no = 6
      end if
C*************************************************************************
C
      Data msize /20/
```

```
C
      write(1,*) 'ENTER NUMBER OF RUNS'
      read(1,*) NN
      write(1,*) 'ENTER NUMBER OF DEPENDANT VARIABLES'
      read(1,*) RR
      write(1,*) 'ENTER NUMBER OF PARAMETERS(UNKNOWNS)'
      read(1,*) KK
C
      open (20,FILE= 'Filename')
      STinv = 0.
      do 400 i = 1,NN
c     write(1,*) 'ENTER # OF THE RUN'
      read(20,'(a10)', END = 1100, ERR = 1100) Rn
      iend = index(Rn,' ')
      Rns = Rn(1:iend-1)
      Datafile = 'SG' // Rns // '.DAT'
      open (10,FILE=Datafile)
      read (10,*) Np,TOS
      read (10,*) Mcat,Bt(i),Pr,COpc,Fin,Fout
      read (10,*) H2m,COm,CO2m,H2Om,METm
      read (10,*) (HCm(j) , j = 1,Np)
      close(10)
C
      LO = HCm(2) + HCm(4) + HCm(8) + HCm(10) + HCm(11)
C     Y(i) = -( (1-.01*COpc)*Fin - .01*H2m*Fout ) / Mcat
      Y(i) = -1e12*.01*( COpc*Fin - (COm+CO2m)*Fout ) / Mcat
C     Y(2*NN+i) = .01*CO2m*Fout / Mcat
C     Y(3*NN+i) = .01*LO*Fout / Mcat
C
      Pra = (1. + Pr/14.7)
      X(i) = Bt(i) + 273.15
      X(NN + i)   = .01*CFUG(Pra/ 12.8,X(i)/ 33.2,.0  )*H2m *Pra
      X(2*NN + i) = .01*CFUG(Pra/ 34.5,X(i)/132.9,.041)*COm *Pra
      X(3*NN + i) = .01*CFUG(Pra/ 72.8,X(i)/304.2,.225)*CO2m*Pra
      X(4*NN + i) = .01*CFUG(Pra/ 79.9,X(i)/512.6,.556)*METm*Pra
      X(5*NN + i) = .01*CFUG(Pra/217.6,X(i)/647.1,.348)*H2Om*Pra
      X(6*NN + i) = .01*CFUG(Pra/ 40.0,X(i)/320.0,.100)*LO  *Pra
      X(7*NN + i) = TOS
C
      Tinv(i) = 1./ X(i)
      STinv = STinv+Tinv(i)
 400  continue
      close(20)
      Tav = STinv/NN
c     do i = 1,NN
c     X(i) = Tinv(i) - Tav
c     end do
C     write(1,'('' ENTER ACTIVITY COEFFICIENT OR CUMULATIVE TIME ON STRE
C    $AM '' / '' FOR EACH RUN, IN RIGHT ORDER '')' )
c     read(1,*) (X(7*NN + i) , i = 1,NN)
c
      open (30, FILE = 'estim.dat')
c     write(1,*) 'ENTER INITIAL GUESSES OF PARAMETER VALUES(IN RIGHT OR
c    1DER)'
      read(30,*) (B(i) , i =1,KK)
```

```
c     read (1,*) (B(i) , i =1,KK)
c     write (1,*) 'ENTER MINIMUM VALUES OF PARAMETERS'
      read(30,*) (BMIN(i) , i = 1,KK)
c     read (1,*) (BMIN(i) , i = 1,KK)
c     write (1,*) 'ENTER MAXIMUM VALUES OF PARAMETERS'
      read(30,*) (BMAX(i) , i = 1,KK)
c     read (1,*) (BMAX(i) , i = 1,KK)
      close (30)
C
      FNU = 0.0
      FLA = 0.0
      TAU = 0.0
      EPS = 0.0
      PHMIN = 0.0
      I = 0
      KD = KK
      FV = 0.0
      DO J = 1, KK
          BV(J) = 1
      END DO
      ICON = KK
      ITER = 0
      WRITE (NO,15)
15    FORMAT ( 10X,27HBSOLVE REGRESSION ALGORITHM)
      NN = NN*RR
      Iterd = 0
C
200   CALL BSOLVE(KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,DV,BV,
     $P,FUNC,DERIV,KD,GAMM,Cov,RR,CFUG)
C
      ITER = ITER + 1
      WRITE (NO,1) ICON, PH, ITER
1     FORMAT (9X,6HICON = , I3, 4X, 5HPH = , E15.8, 4X,
     $16HIteration No. = , I3)
      If (Iter.eq.(Iterd + 200)) then
          Iterd = Iter
          do j= 1,KK
          write(1,3) j, B(j)
          enddo
      end if
      IF (ICON) 10, 300, 200
10    IF (ICON+1) 20, 60, 200
20    IF (ICON+2) 30, 70, 200
30    IF (ICON+3) 40, 80, 200
40    IF (ICON+4) 50, 90, 200
50    GO TO 95
60    WRITE (NO,4)
4     FORMAT (//, 9X, 32HNo Function Improvement Possible )
      GO TO 300
70    WRITE (NO,5)
 5    FORMAT (//,9X, 28HMore Unknowns than Functions)
      GO TO 300
80    WRITE (NO, 6)
6     FORMAT (//,9X, 2HTotal Variables are Zero)
      GO TO 300
```

```
90    WRITE (NO,7)
7     FORMAT (//,9X,79HCorrections Satisfy Convergence Requirements but
     $Lamda Factor (FLA) still Large)
      GO TO 300
95    WRITE (NO,8)
8     FORMAT (//,9X, 20HThis is not Possible)
      GO TO 300
300   WRITE (NO,2)
2     FORMAT (//,9X, 26HSolutions of the Equations)
      DO J = 1, KK
          WRITE(NO,3) J, B(J)
      END DO
3     FORMAT (/,9X, 2HB(, I2, 4H) = , E12.4)
c
c**************************************************************************
c   Inversion of matrix Cov= Transf(Jacobian)*Jacobian
c************************************************************************
c
c      call invrt(Cov,msize,kk,ipvt,ierr)
c
c************************************************************************
c                        Result Printing
c************************************************************************
c
      NN = NN/RR
      open(30,FILE='filename')
      do i =1,NN
         read(30,'(a7)') Rid(i)
      enddo
      close(30)
      write(NO,500)
  500 format(//,1x,30x,5'*',1x,'PRESSURES (atm)',1x,5'*'//
     $        1x,2x,'RUN',11x,'H2',10x,'CO',9x,'CO2',8x,
     $'METOH',8x,'H2O',9x,'LO'/)
      do i = 1,NN
      write(NO,501) Rid(i), X(i+NN),X(i+2*NN),X(i+3*NN),X(i+4*NN),
     $              X(i+5*NN),X(i+6*NN)
      end do
  501 format(1x,a7,4x,5(e8.3,4x),e8.3 )
      write(NO,502)
  502 format(//,1x,17x,5'*','RATES (umoles/(sec.gcat.)',1x,5'*'//
     $        1x,3x,'RUN',22x,'H2',33x,'CO',/)
      write(NO,509)
      do i = 1,NN*RR
C     Y(i) = exp( Y(i) )
C     Z(i) = exp( Z(i) )
      Err(i) = 100.*(Z(i) - Y(i))/ Z(i)
      end do
      do i = 1,NN
      write(NO, 510) Rid(i),Y(i),Z(i),Err(i),Y(i+NN),Z(i+NN),Err(i+NN)
      end do
      write(NO,503)
  503 format(//,1x,3x,'RUN',22x,'CO2',26x,'Light Olefins',/)
      write(NO,509)
      do i= 1,NN
      write(NO,510) Rid(i),Y(i+2*NN),Z(i+2*NN),Err(i+2*NN),
     $                    Y(i+3*NN),Z(i+3*NN),Err(i+3*NN)
      enddo
  509 format(1x,10x,2(5x,'Exp.',8x,'Calc.',5x,'Err(%)',2x),/)
  510 format (1x,a7,3x,2(2x,e8.2,6x,e8.2,5x,f5.2,2x))
      write(NO,512)
  512 format(//,1x,17x,5'*', '(PH2*PCO2/PCO/PH2O) / KWGS',5'*' ,/
     $          1x 2x,'RUN',7x,'BETA',7x,'KWGS',8x,'KPWGS',/ )
      do i = 1,NN
      write(NO,513) Rid(i),BETA(i) ,KWGS(i) ,KPWGS(i)
      enddo
  513 format(1x,a7,5x,e7.2,5x,e7.2,5x,e7.2)
c
c     write(NO,515) Tav
c515  format(/,3x,'1/T AVERAGE=',e9.3,1x,'(1/K)',//)
c
c     write(NO,517)
c517  format(//,1x,4x,3'*','VARIANCE-COVARIANCE MATRIX OF PARAMETER ESTI
c    $                         MATES',3'*',/)
c     do i = 1,KK
c     write(NO,520) (cov(i,j), j=1,KK)
c520  format(1x,20(e9.2,3x))
c     end do
C***********************************************************************
C
C                 UNLOCKING THE PRINTER (IO 6)
C***********************************************************************
      write(NO,530)
 530  format('1')
      OPTION = 140000B
      CALL LURQ (OPTION,LUARY,NUMLUS)
C
1100  Write(1,'(''   You have to create a file named FILENAME  which con
     $tains the identification'' / '' part (id) in the names of the data
     $files.'' // ''   For example, for the datafile SG880621A.dat, you
     $enter in FILENAME : 880621A'' // ''   Only one datafile id  is ent
     $ered per record (or line ) of FILENAME .'')' )
C
1000  STOP
      END
C     *****************************************************************
      SUBROUTINE FUNC ( KK, B, NN, RR, Z, FV, CFUG )
C
      DIMENSION X(350), Z(100), B(25)
      Dimension BETA(50), Xinv(50)
      Integer RR
      Real KPMS,KFMS,KMS,KPWGS(50),KFWGS,KWGS(50),Num
      COMMON X ,BETA ,Pra ,KWGS,KPWGS,Tav
C
      NN = NN/RR
      DO JJ = 1, NN
c
c*********************************************************************
c           Equilibrium Constant for Methanol Synthesis Reaction
c*********************************************************************
```

```
      KPMS = -9.09 - 24.24e3*(X(JJ)-600)/600/X(JJ)/1.987
      KPMS = exp(KPMS)
      KFMS = CFUG(Pra/79.9,X(JJ)/512.6,.556)/
     $       CFUG(Pra/34.5,X(JJ)/132.9,.041)/
     $       CFUG(Pra/12.8,X(JJ)/ 33.2,.0)**2
      KMS = KFMS*KPMS
c*******************************************************************
c                Equilibrium Constant for the WGS Reaction
c*******************************************************************
      KPWGS = 3.296 - 9.17e3*(X(JJ)-600)/600/X(JJ)/1.987
      KPWGS(JJ) = exp(KPWGS)
      KFWGS = CFUG(Pra/ 72.8,X(JJ)/304.2,.225) *
     $        CFUG(Pra/ 12.8,X(JJ)/ 33.2,0.0 ) /
     $        CFUG(Pra/ 34.5,X(JJ)/132.9,.041) /
     $        CFUG(Pra/217.6,X(JJ)/647.1,.348)
      KWGS(JJ) = KFWGS*KPWGS(JJ)
c*******************************************************************
c
      Xinv(JJ) = 1./X(JJ) - Tav
c
c*******************************************************************
c        Kinetic Rate of the Methanol Synthesis Reaction
c*******************************************************************
      Num = X(JJ+2*NN)*X(JJ+NN)**2 - X(JJ+4*NN)/KMS
C     Bco = 1.33E-10 * EXP( 23850/1.987/X(JJ) )
      Bco = B(3) * exp( B(4)*Xinv(JJ)/1.987 )
C     C = 4.72E-14 * EXP( 30500/1.987/X(JJ) )
      C = B(5) * exp( B(6)*Xinv(JJ)/1.987 )
C     D = 5.05E-12 * EXP( 31250/1.987/X(JJ) )
      D = B(7) * exp( B(8)*Xinv(JJ)/1.987 )
C     E = 3.33E-10 * EXP( 23850/1.987/X(JJ) )
      Denom = 1 + Bco*X(JJ+  NN) + C*X(JJ+2*NN) + D*X(JJ+3*NN)
C    $          + B(4)*X(JJ+3*NN)
      A = exp(B(9)*X(JJ+7*NN)) /((B(1)*exp( B(2)*Xinv(JJ)/1.987)))**3
c     A = exp(B(5)*X(JJ+7*NN)) /(B(1))**3
      RMSC = A * Num / (Denom)**3
c*******************************************************************
c                  Kinetic Rate of the WGS reaction
c*******************************************************************
      BETA(JJ) = X(JJ+NN)*X(JJ+3*NN)/X(JJ+2*NN)/X(JJ+5*NN)
     $                                        /KWGS(JJ)
C     RWGS = B(2) * X(JJ+  NN)**B(3) * X(JJ+2*NN)**B(4)
C    $            * X(JJ+3*NN)**B(5) * X(JJ+5*NN)**B(6)
C    $            * ( 1-BETA(JJ) )
c*******************************************************************
c      Predicted Rates for H2,CO consumptions and CO2 Formation
c                          (in this order)
c*******************************************************************
C     Z(JJ) = -2*RMSC + RWGS
      Z(JJ) = -1e12*RMSC
C     Z(2*NN+JJ) = RWGS
c
      END DO
      NN = NN*RR
      RETURN
      END
C************************************************************************
C                         Fugacity Coefficients
C************************************************************************
      FUNCTION CFUG (Pr,Tr,Omega)
      B0 = .083 - .422/(Tr)**1.6
      B1 = .139 - .172/(Tr)**4.2
      CFUG = exp( (B0 + Omega*B1)* Pr/Tr )
      return
      end
```

APPENDIX F

FISCHER-TROPSCH CONVERSION OF SYNGAS TO HYDROCARBONS ON CANMET #112 CATALYST:

- calculation of conversions, mass balances and product distribution
- Printout of the results (for Run SG880812B)

```
                  ****************************************
                  *                                      *
                  *     SYNTHESIS GAS CONVERSION RUN     *
                  *                                      *
                  *             SG880812B                *
                  *                                      *
                  ****************************************


****************************
    OPERATING CONDITIONS
****************************

                TEMPERATURE: 272.0 oC
                   PRESSURE:  16.3 atm
                H2/CO ratio:   .97
             FEED FLOW RATE:  60.0 .
                       WHSV: 479. mlSTP/gcat/hr
              TEST DURATION: 142. minutes
   CUMULATIVE TIME ON STREAM: 512. hours

********************
    CONVERSIONS
********************

  CO CONVERSION:  8.0 %
  H2 CONVERSION: 11.5 %

***************************************
    PRODUCT MASS DISTRIBUTION (WT%)
***************************************

            CO2      36.13
            H2O      29.28
            HC       34.59
            METOH     0.00

***********************
     MASS BALANCE
***********************

                     OUT - IN (ugram/sec)    %ERROR

      CARBON:                  -6.7           -1.8
    HYDROGEN:                   0.0            0.0
      OXYGEN:                  -7.7           -1.6

       TOTAL:                 -14.4           -1.7
```

```
*****LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION*****

COMPOUND                                WEIGHT % OF TOTAL HYDROCARBONS


Methane                                              34.34
Ethylene                                              2.23
Ethane                                               16.11
Propylene                                             8.39
Propane                                               7.98
C4 paraffins                                          6.93
C4 olefins                                            7.97
C5 paraffins                                          3.61
C5 olefins                                            4.23
C6 paraffins                                          1.99
C6 olefins                                            1.64
C7                                                    1.82
C8                                                    1.10
C9                                                     .48
C10                                                    .37
C11                                                    .19
C12                                                    .15
C13                                                    .12
C14                                                    .21
C15                                                    .07
C16                                                    .07
```

```
          ***TOTAL HYDROCARBON MASS DISTRIBUTION***

NUMBER              NAME                TOTAL HC %


  1 Methane                              34.339
  2 Ethylene                              2.231
  3 Ethane                               16.110
  4 Propylene                             8.394
  5 Propane                               7.983
  6 I-Butane                              0.000
  7 C4                                    1.602
  8 1-Butene                              2.967
  9 N-Butane                              6.926
 10 ?                                     0.000
 11 2-Butane                              1.829
 12 2-Butane                              1.569
 13 C5-Unsaturate(C5H10)                  0.000
 14 C5-Unsaturate(C5H10)                   .118
 15 I-Pentane(C5H12)                       .905
 16 C5H10                                  .429
 17 C5H10                                  .252
 18 C5H10                                 1.075
 19 C5H10                                  .107
 20 N-Pentane-C5H12                       2.705
 21 C5H10                                 1.211
 22 C5H10                                  .694
 23 C5H10                                  .238
 24 C5H10                                  .055
 25 C5H10                                  .056
 26 C6-Unsat-C6H12                         .091
 27 Dimethyl Butane                       0.000
 28 C6H12                                  .037
 29 2-Methyl-Pentane                       .199
 30 C6H12                                  .036
 31 C6H12                                 0.000
 32 C6H12                                 0.000
 33 3-Methyl Pentane                       .209
 34 C6H12                                  .380
 35 N-Hexane                              1.586
 36 C6H12                                  .150
 37 C6H12                                  .540
 38 C6H12                                  .053
 39 C6H12                                 0.000
 40 C6H12                                  .328
 41 Methyl Cyclo Pentane(?)                .026
 42 C6H12                                 0.000
 43 C7H16                                  .046
 44 C7H16                                 0.000
 45 Dimethyl Pentane                      0.000
 46 C7H16                                  .081
 47 C7H16                                  .099
 48 C7H16                                 0.000
 49 C7H16                                  .143
 50 C7H16                                 1.057
 51 C7H16                                 0.000
```

52	C7H16	.242
53	C7H16	.151
54	C8	0.000
55	C8	.030
56	C8	0.000
57	C8	.073
58	C8	.059
59	C8	.069
60	C8	.671
61	C8	.128
62	C8	.068
63	C9	0.000
64	C9	0.000
65	C9	0.000
66	C9	.413
67	C9	.063
68	C10	0.000
69	C10	0.000
70	C10	.108
71	C10	.262
72	C11	0.000
73	C11	.187
74	C12	.150
75	C13	.120
76	C14	.206
77	C15	.075
78	C16	.066

```
               **************************************
               *                                    *
               *     SYNTHESIS GAS CONVERSION RUN   *
               *                                    *
               *             SG880812B              *
               *                                    *
               **************************************



 Catalyst : CANMET #112
                         *****TCD ANALYSIS RESULTS*****

-----------------------------------------------------------------------------
 TIME (min)                18.0       34.0       132.0
 H2/CO                      1.0        1.0         1.0
 P (psig)                 225.0      225.0       225.0
 T (oC)                   272.0      272.0       272.0
 MFC setpoint               5.0        5.0         5.0
 FLOW(mmole/gr.cat)          .3         .3          .3
-----------------------------------------------------------------------------
 CO conv (%)                9.9       10.2         8.5
 H2 conv (%)               14.8       14.8        12.0
-----------------------------------------------------------------------------
Product mass distribution

    CO2                    37.9       38.3        37.8
    H2O                    28.7       28.4        30.6
 Hydroc.+Oxygenates        33.4       33.3        31.5
-----------------------------------------------------------------------------
Hydrocarbons(+Oxygenates) mass distribution

   CH4                     44.7       44.2        44.8
   C2=                      2.0        2.0         2.3
   C2                      18.0       17.9        17.6
   C3=                     10.4       10.0        10.5
   C3                       8.4        8.9         8.0
   C4s                     10.6       11.1        10.9
   C5+                      5.9        5.9         5.8
   METOH                    0.0        0.0         0.0
-----------------------------------------------------------------------------
Mass Balance

 CO+H2conv.(mg/min)         5.6        5.8         4.8
 Prod. mass(mg/min)         4.6        4.3         3.5
 Loop vol. bypa(ul)      1024.4     1024.4      1024.4
 Loop vol.     (ul)      1023.4     1018.3      1026.0
 CO feed    (mole%)        50.9       50.9        50.9
-----------------------------------------------------------------------------
```

```
CATALYST WEIGHT=  10.90 grams

TOTAL RUN TIME =142. min

CORRECTION FACTORS FOR THE HYDROCARBON FRACTION NOT   DETECTED
IN THE TCD ANALYSIS CALCULATED WITH :
           C1                       C2                      C3

         .6214                    .1713                   .2674

           FLOW RATES AT THE EXIT OF THE REACTOR (ml STP/min)

  NON CONDENSED    TOTAL,ESTIMATED FROM FLOW RATE   TOTAL,ESTIMATED FROM MASS
  HYDROCARBONS           AFTER CONDENSOR             OF CONDENSED LIQUIDS

    81.30                                                   81.87

AVERAGE MOLECULAR WEIGHT OF HYDROCARBON FRACTIONS:  27.79

                         *****CONVERSIONS (%)*****

                  H2                                   CO

                11.5                                    8.0

                    *****MASS BALANCES (ugram/sec)*****

   ON OXYGEN      ON CARBON     ON HYDROGEN  CONVERTED MASS  PRODUCED MASS

     -7.69          -6.71           0.00          75.45             60.35
     -1.6%          -1.8%          0.00%


                 *****BULK PRODUCT MASS DISTRIBUTION(WT%)*****

        CO2                H2O          HYDROCARBONS        CH3OH

       36.13             29.28             34.59              0.001
```

APPENDIX G

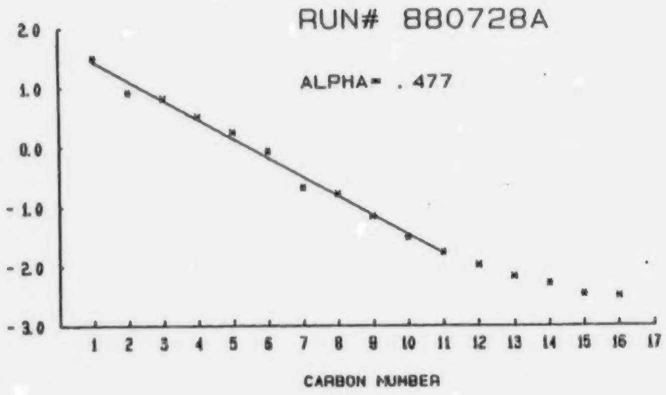
FISCHER-TROPSCH CONVERSION OF SYNGAS TO HYDROCARBONS ON CANMET #112 CATALYST:

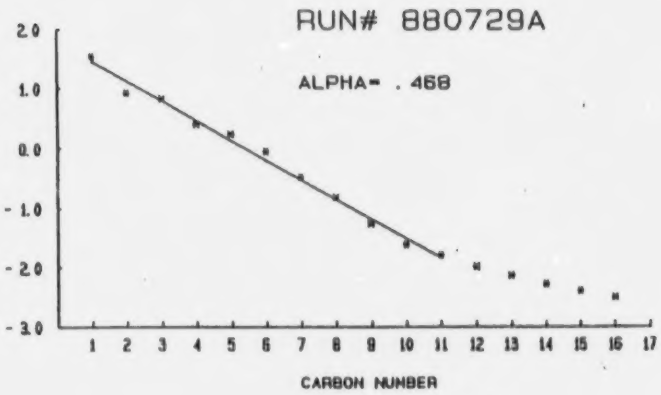
- calculation of the SCHULZ-FLORY-ANDERSON hydrocarbon product distributions
- Listing of program SCHULZ
- Plots of the SCHULZ-FLORY-ANDERSON distributions for each kinetic run

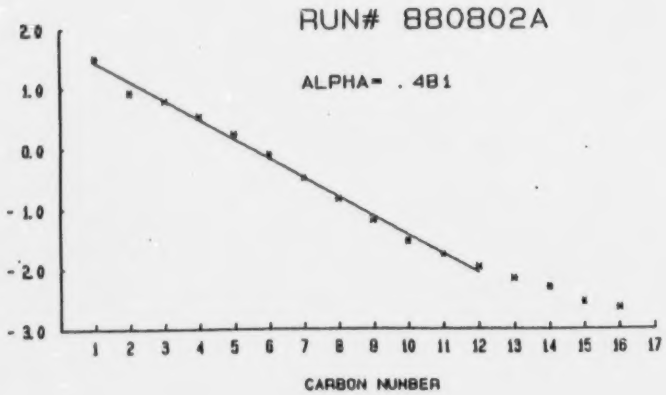
```
FTN7X,L,S
$CDS ON
$FILES 0,2
      PROGRAM SCHULZ
C     IAN PARROTT-NOVEMBER 16, 1988
C     THIS PROGRAM CALCULATES THE PARAMATERS IN THE SCHULZ-FLORY
C     DISTRIBUTION FOR THE CANMET 112 CATALYST.
C     THE DATA FILE CONTAINS THE MASS FRACTION OF EACH COMPOUND BY
C     CARBON NUMBER
C
C     C(I)=CARBON NUMBER;CS(I)=C**2,SCS(I)=SUM OF CS
C     MC(I)=MASS FRACTION OF I;Y(I)=LOG[M/C],SY=SUM OF Y(I)
C     SCY=SUM OF C(I)*Y(I)
C
      REAL LTHC(21),C(16),CS(16),SCS,SC,Y(16),CY(16),SCY,SY
      REAL A,B,ALPHA,Q(16),SQ,MC(16),YS(16)
      REAL CTOS,MCAT,TA,PA,COPCA,FIN,FOUT2,H2M,COM,CO2M,H2OM,METM
      REAL HCM(100),SXX,SYY,SXY,R2
      INTEGER I,N,NXTIC,NYTIC,NIX,NDX,NIY,NDY,CONTRL,IERR,NC,CODE,ALP(2)
      INTEGER BASE(2)
      CHARACTER*24 NAME1,NAME2
C
      REAL XMIN,XSTA,XEND,XMAX,XSP
      REAL YMIN,YSTA,YEND,YMAX,YSP
      REAL WIDTH, HEIGHT
      COMMON /XAXIS/ XMIN,XSTA,XEND,XMAX,NXTIC,NIX,NDX,XSP
      COMMON /YAXIS/ YMIN,YSTA,YEND,YMAX,NYTIC,NIY,NDY,YSP
      COMMON /FBACK/ WIDTH, HEIGHT
C
C     READ THE MASS DISTRIBUTION FROM THE DATA FILES
C     DATA FILES='CANMETrun#'
C
      SCS=0.0
      SC=0.0
      SCY=0.0
      SY=0.0
      SQ=0.0
      CALL FPARM(NAME1)
      OPEN(10,FILE=NAME1)
      READ(10,*) N,CTOS
      READ(10,*) MCAT,TA,PA,COPCA,FIN,FOUT2
      READ(10,*) H2M,COM,CO2M,H2OM,METM
      READ(10,*) (HCM(I), I=1,N)
      READ(10,*) (LTHC(I), I=1,21)
      CLOSE(10)
C
C     OBTAIN THE MASS DISTRIBUTION ACCORDING TO CARBON NUMBER
C
      MC(1)=LTHC(1)
      MC(2)=LTHC(2) + LTHC(3)
      MC(3)=LTHC(4) + LTHC(5)
      MC(4)=LTHC(6) + LTHC(7)
      MC(5)=LTHC(8) + LTHC(9)
      MC(6)=LTHC(10) + LTHC(11)
      DO 10 I=7,16
```

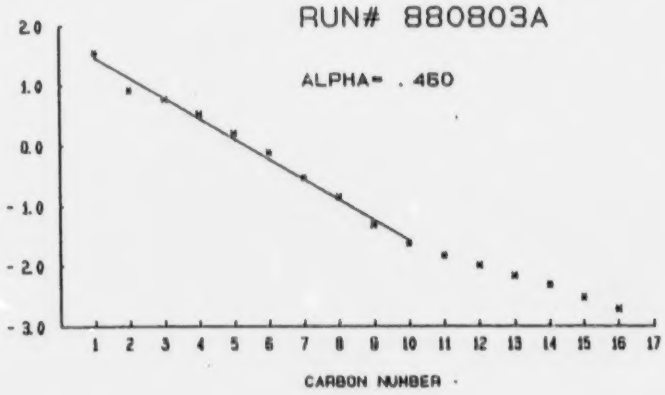
```
         MC(I) = LTHC(I+5)
   10 CONTINUE
      DO 11 I=1,16
         C(I)=I
   11 CONTINUE
C
C     CALCULATE THE SUMS AND PRODUCTS NEEDED FOR THE LINEAR
C     REGRESSION ANALYSIS.
C
      WRITE(1,*) 'ENTER THE HIGHEST CARBON NUMBER'
      READ(1,*) NC
      DO 15 I=1,NC
          CS(I)=C(I)*C(I)
          SCS=SCS+CS(I)
          SC=SC+C(I)
          Y(I)=LOG10(MC(I)/C(I))
          YS(I)=Y(I)*Y(I)
          SYS=SYS+YS(I)
          CY(I)=C(I)*Y(I)
          SCY=SCY+CY(I)
          SY=SY+Y(I)
   15 CONTINUE
C
C     USE LINEAR REGRESSION TO CALCULATE THE SLOPE AND INTERCEPT
C     OF THE STRAIGHT LINE
C
      B=(SY*SCS-SCY*SC)/(NC*SCS-SC*SC)
      A=(SY-NC*B)/SC
C
C     CALCULATE THE PROBABILTIY OF CHAIN GROWTH
C     AND THE REGRESSION ERROR
C
      ALPHA=10**A
      SXX=NC*SCS-SC**2
      SYY=NC*SYS-SY**2
      SXY=NC*(SCY)-SC*SY
      R2=SXY/(SXX*SYY)**.5
C
      DO 22 I=1,16
         Y(I)=LOG10(MC(I)/C(I))
   22 CONTINUE
C
C     PRINT OUT THE RESULTS
C
      WRITE(1,*) 'OUTPUT DESTINATION'
      WRITE(1,*) 'SCREEN<1>'
      WRITE(1,*) 'OUTPUTFILE<2>'
      READ(1,*) NO
      NAME2='SCHULZ'//NAME1(7:17)
      OPEN(20,FILE=NAME2)
      IF(NO.EQ.2) THEN
         NO=20
      ENDIF
      WRITE(NO,500)
  500 FORMAT('RESULTS OF SHULZ-FLORY DISTRIBUTION ANALYSIS')
```

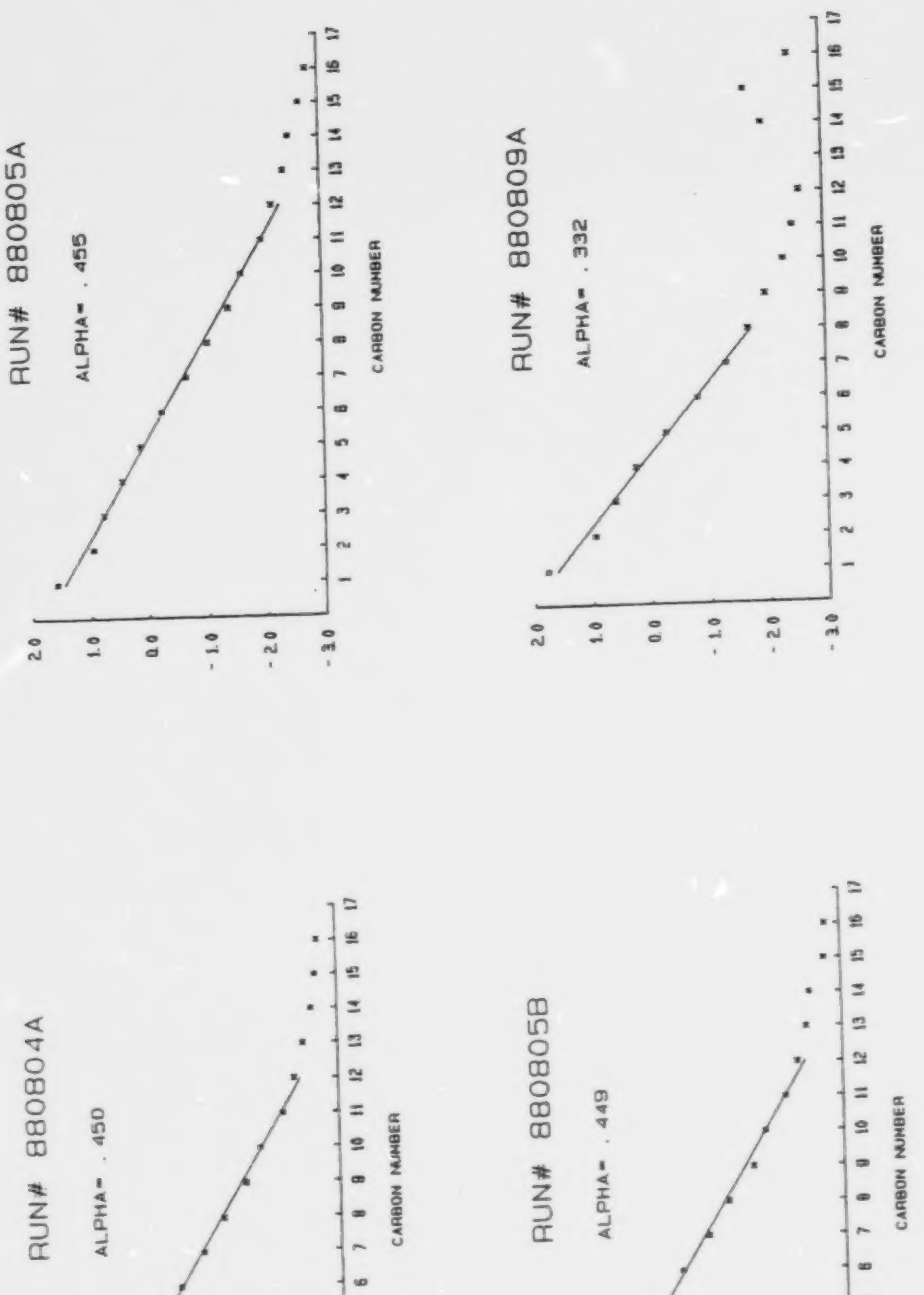
```
      WRITE(NO,501) A
  501 FORMAT(//'SLOPE=',1X,F10.3)
      WRITE(NO,502) B
  502 FORMAT('INTERCEPT=',1X,F10.3)
      WRITE(NO,503) ALPHA
  503 FORMAT('PROBABILITY OF CHAIN GROWTH=',1X,F5.3)
      WRITE(NO,504) R2
  504 FORMAT('CORRELATION FACTOR=',1X,F5.3)
      WRITE(NO,505)
  505 FORMAT(/,'LOG[M/C]',5X,'CARBON NUMBER',/)
      DO 510 I=1,16
         WRITE(NO,506) Y(I),C(I)
  510 CONTINUE
  506 FORMAT(F10.4,5X,F10.4)
      CLOSE(20)
C
C     PLOT THE GRAPH
C
      CALL ZBEGN
      CALL ZDINT(6,CONTRL,IERR)
      CALL ZASPK(1.0,0.6)
      CALL ZDLIM(15.,235.,15.,180.)
C
      BASE(1) = 1
      BASE(2) = 1
      SIZE = 0.5
C
      XMIN=-1.5
      XSTA=0.
      XEND=17.
      XMAX=20.
      NXTIC=17
      NIX=2
      NDX=0
C
      YMIN=-5.0
      YSTA=-3.0
      YEND=2.0
      YMAX=2.5
      NYTIC=5
      NIY=2
      NDY=1
C
      CALL ZVIEW(0.,.6,0.0,1.)
      CALL ZWIND(XMIN,XMAX,YMIN,YMAX)
      CALL ZAXES(SIZE, BASE)
      DO 600 I=1,16
         CALL ZMOVE(C(I),Y(I))
         CALL ZMARK(3)
  600 CONTINUE
      D1=A*C(1) + B
      D2=A*C(NC) + B
      CALL ZMOVE(C(1),D1)
      CALL ZDRAW(C(NC),D2)
      CALL ZMOVE(7.0,-4.0)
      CALL ZCSIZ(.3,.3)
      CALL ZTEXT(13,13HCARBON NUMBER)
      ENCODE(7,520,CODE) NAME2(7:13)
  520 FORMAT(A7)
      CALL ZCSIZ(.6,.6)
      CALL ZMOVE(7.0,2.0)
      CALL ZTEXT(5,5HRUN# )
      CALL ZTEXT(7,CODE)
      INT=ALPHA*1000
      ENCODE(3,521,ALP) INT
  521 FORMAT(I3)
      CALL ZCSIZ(.4,.4)
      CALL ZMOVE(7.0,1.0)
      CALL ZTEXT(8,8HALPHA= .)
      CALL ZTEXT(4,ALP)
      CALL ZEND
      STOP
      END
```

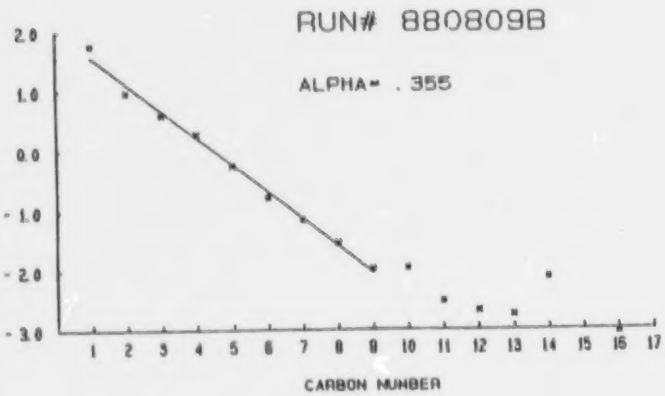

RUN# 880728A
ALPHA= . 477
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

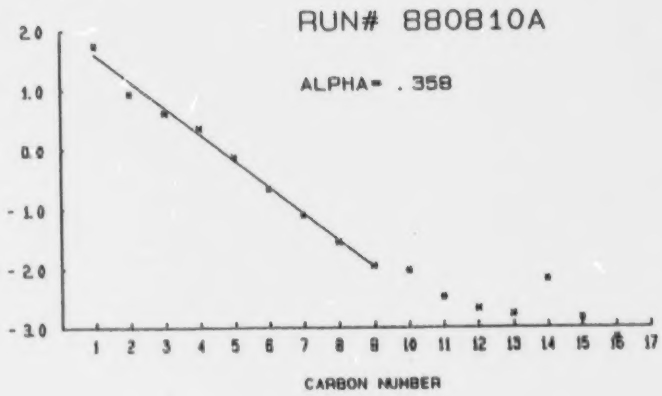

RUN# 880729A
ALPHA= . 468
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

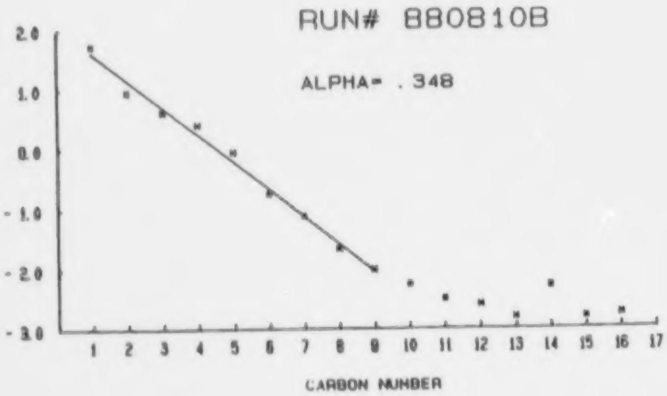

RUN# 880802A
ALPHA= . 481
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

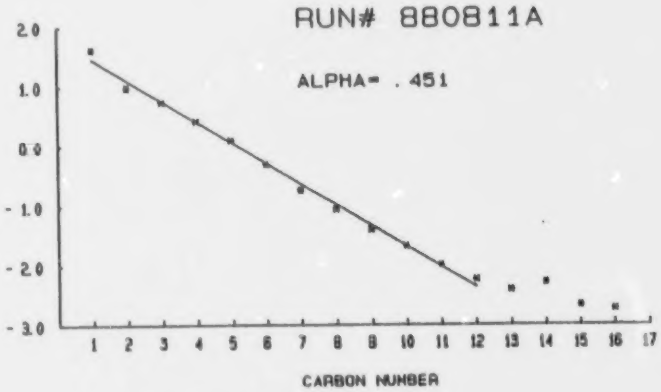

RUN# 880803A
ALPHA= . 460
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

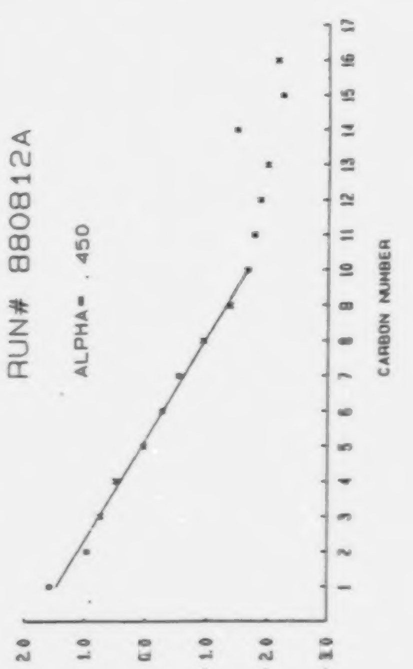

RUN# 880804A
ALPHA= . 450
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER
RUN# 880805A
ALPHA= . 455
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER
RUN# 880805B
ALPHA= . 449
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER
RUN# 880809A
ALPHA= . 332
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

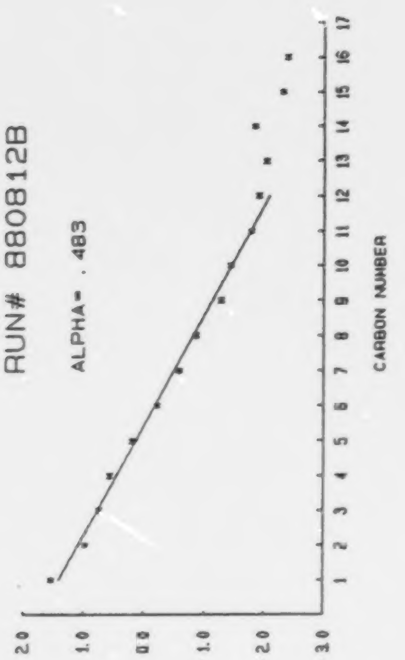

RUN# 880809B
ALPHA= .355
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

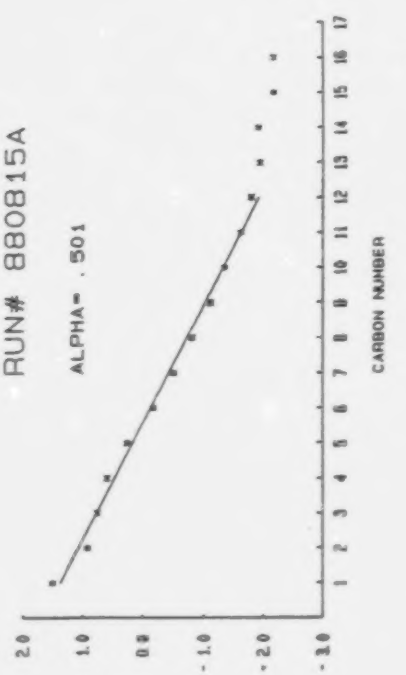

RUN# 880810A
ALPHA= .358
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

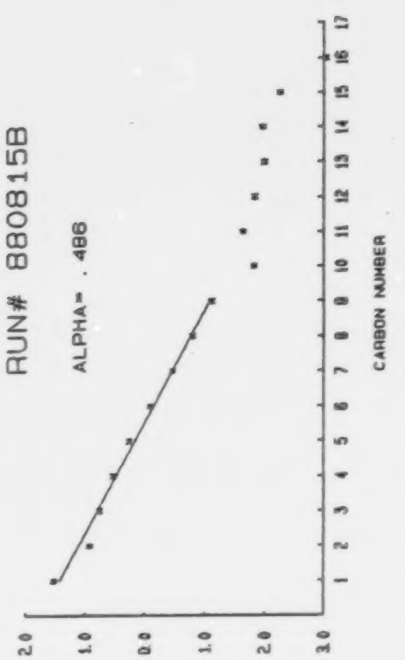

RUN# 880810B
ALPHA= .348
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

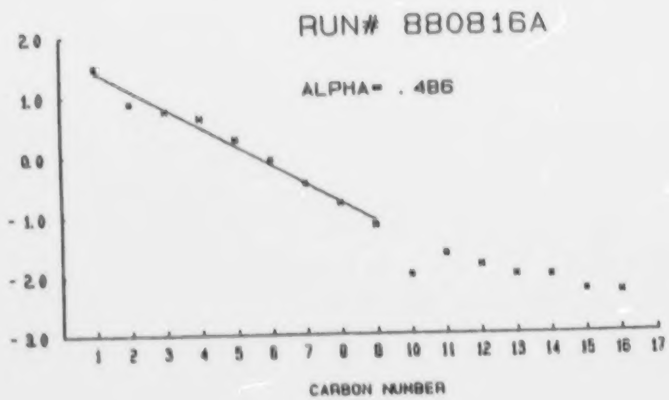

RUN# 880811A
ALPHA= .451
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

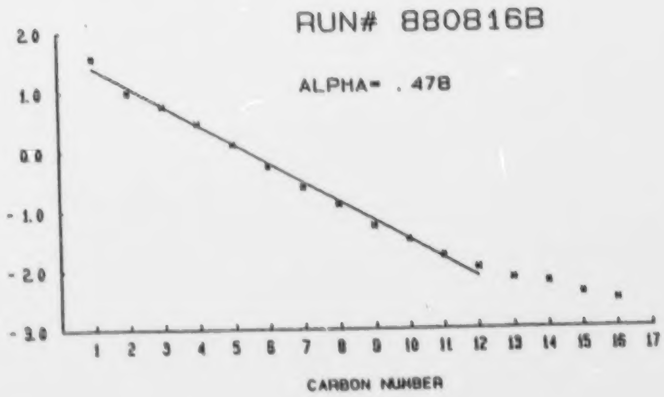

RUN# 880812A
ALPHA= .450
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

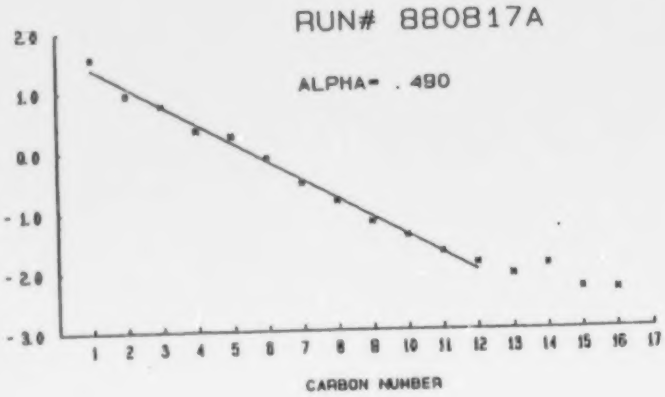

RUN# 880812B
ALPHA= .483
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

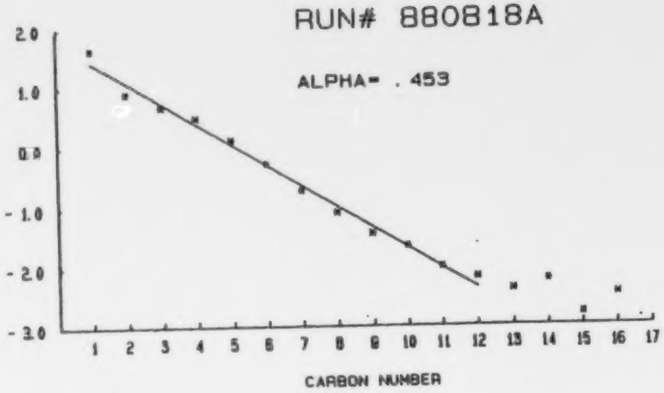

RUN# 880815A
ALPHA= .501
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

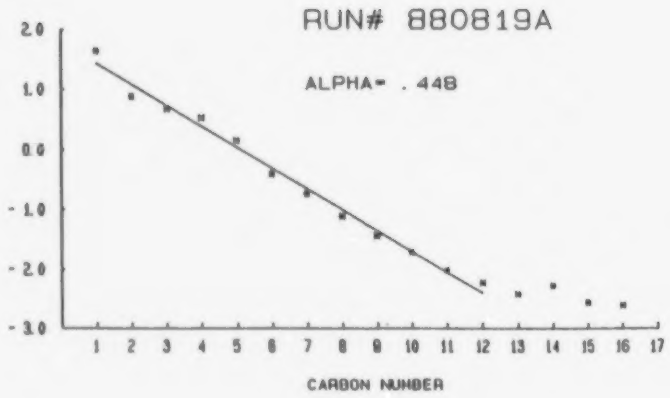

RUN# 880815B
ALPHA= .486
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

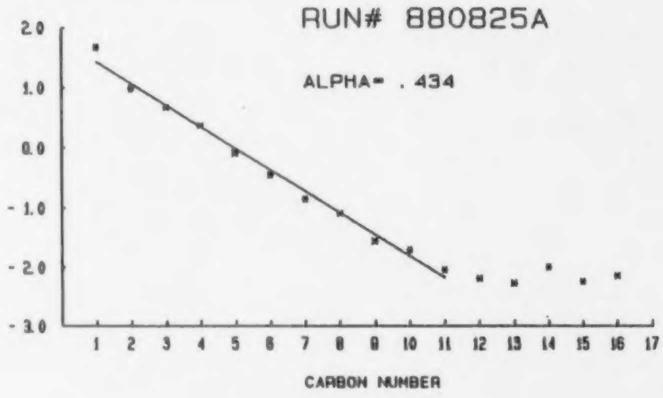

RUN# 880816A
ALPHA= . 486
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

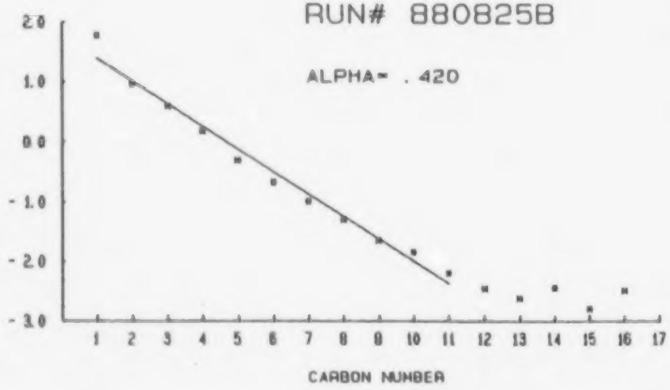

RUN# 880816B
ALPHA= . 478
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

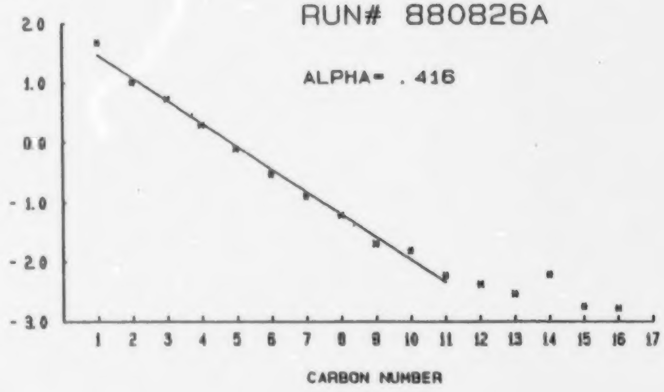

RUN# 880817A
ALPHA= . 490
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

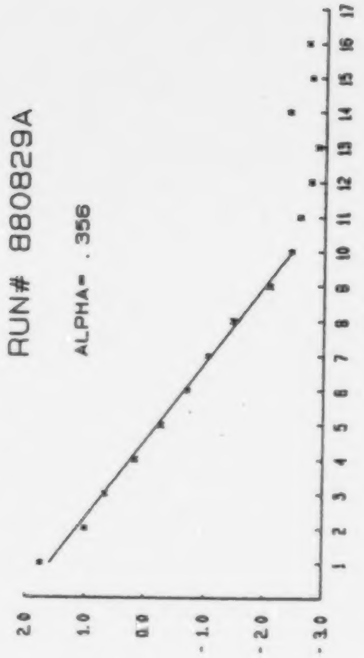

RUN# 880818A
ALPHA= . 453
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

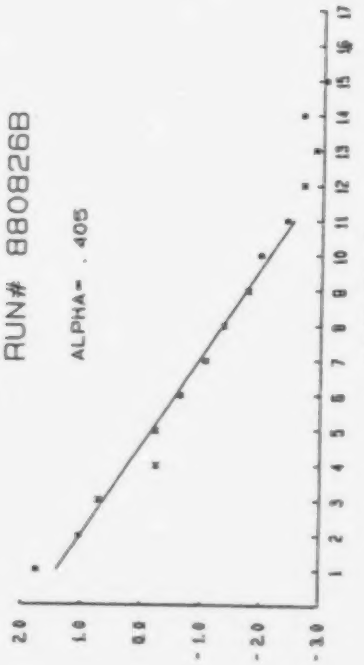

RUN# 880819A
ALPHA= . 448
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

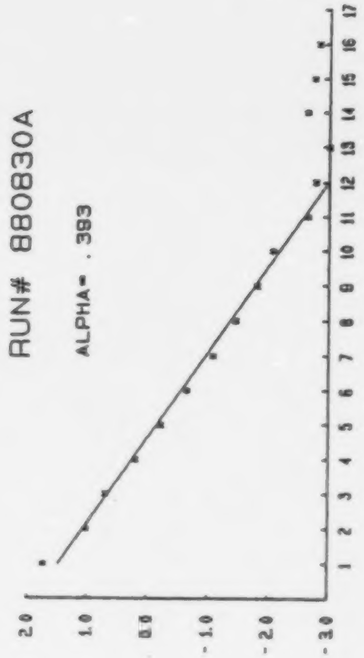

RUN# 880825A
ALPHA= . 434
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER

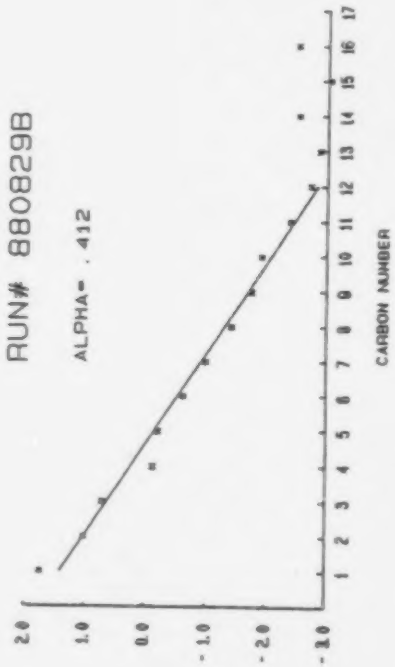

RUN# 880825B
ALPHA= . 420
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER


RUN# 880826A
ALPHA= . 416
2.0
1.0
0.0
- 1.0
- 2.0
- 3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
CARBON NUMBER


RUN# 880829A
ALPHA= . 356
CARBON NUMBER
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17


RUN# 880826B
ALPHA= . 405
CARBON NUMBER
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17


RUN# 880830A
ALPHA= . 383
CARBON NUMBER
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17


RUN# 880829B
ALPHA= . 412
CARBON NUMBER
2.0
1.0
0.0
-1.0
-2.0
-3.0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

Appendix H

Example of mass balance program printout (PO reactor).

```
              ****************************************
              *                                      *
              *     SYNTHESIS GAS CONVERSION RUN     *
              *                                      *
              *              P0880212                *
              *                                      *
              ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 371.3  C
         PRESSURE:  34 atm
         GAS FLOW:  3.27 l/min
   RESIDENCE TIME: 181.7 s
      H2/CO ratio:  .96
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 260 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 41.2 %
  H2 CONVERSION: 26.4 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:   30.76 g

       MASS OF AQUEOUS PHASE:    0.00 g
           COMPOSITION (WT%):    0.00 % WATER
                                 0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2     75.63
             H2O      1.42
             HC      22.95
             METOH    0.00

***********************
     MASS BALANCE
***********************

                    IN (g)      OUT (g)      %ERROR

       CARBON:    215.31      221.73          -2.98
     HYDROGEN:     34.38       32.97           4.11
       OXYGEN:    287.07      301.03          -4.86

        TOTAL:    536.76      555.73          -3.53
```

```
                    *****HYDROCARBON DISTRIBUTION*****


     ***LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUTIONS***

NUMBER               NAME                LIQ HC %  GASEOUS HC %  TOTAL HC %


  1 Methane                               0.000        6.447       2.772
  2 Ethylene                              0.000         .634        .273
  3 Ethane                                0.000       34.175      14.694
  4 Propylene                             0.000         .219        .094
  5 Propane                               0.000       31.505      13.547
  6 Dimethylether                         0.000        0.000       0.000
  7 i-Butane                              0.000        6.858       2.949
  8 1-Butene                              0.000         .103        .044
  9 n-Butane                              0.000        5.221       2.245
 10 2-Butene                              0.000         .051        .022
 11 2-Butene                              0.000        0.000       0.000
 12 i-Pentane                             0.000        3.549       1.526
 13 Cyclopentane(?)                       0.000        0.000       0.000
 14 C5=                                   0.000        0.000       0.000
 15 n-Pentane                             0.000         .612        .263
 16 C5=                                   0.000        0.000       0.000
 17 C5=                                   0.000        0.000       0.000
 18 C5=                                   0.000        0.000       0.000
 19 Unknown                               0.000         .057        .025
 20 Dimethyl-Butane                       0.000         .219        .094
 21 2,Methyl-Pentane                      0.000         .188        .081
 22 3,Methyl-Pentane                      0.000         .261        .112
 23 C6=                                   0.000        0.000       0.000
 24 n-Hexane                              0.000        0.000       0.000
 25 C6=                                   0.000        0.000       0.000
 26 C6=                                   0.000        0.000       0.000
 27 C6=                                   0.000        0.000       0.000
 28 C6=                                   0.000        0.000       0.000
 29 C6=                                   0.000        0.000       0.000
 30 Methyl-Cyclopentane                   0.000         .096        .041
 31 4-Methyl,1-Pentene(?)                 0.000        0.000       0.000
 32 Unknown                               0.000        0.000       0.000
 33 Benzene                                .049         .234        .129
 34 Cyclohexane                           0.000        0.000       0.000
 35 2,3-Dimethyl-Pentane                  0.000        0.000       0.000
 36 3-Methyl-Hexane                       0.000        0.000       0.000
 37 Dimethyl-Cyclopentane                 0.000        0.000       0.000
 38 Dimethyl-Cyclopentane                 0.000        0.000       0.000
 39 Dimethyl-Cyclopentane                  .009        0.000        .005
 40 Dimethyl-Cyclopentene                 0.000        0.000       0.000
 41 Unknown                               0.000        0.000       0.000
 42 Methyl-Cyclohexane                     .075         .095        .084
 43 1,1,3-Trimethyl-Cyclopentane          0.000        0.000       0.000
 44 4-Methyl-Heptane(?)                    .011        0.000        .006
 45 1,2,4-Trimethyl-Cyclopentane          0.000        0.000       0.000
 46 1,2,3-Trimethyl-Cyclopentane           .012        0.000        .007
 47 C8 Cycloolefin(?)                     0.000        0.000       0.000
```

48	Toluene	1.192	.525	.905
49	C8=(?)	0.000	0.000	0.000
50	C8=(?)	0.000	0.000	0.000
51	C8=(?)	0.000	0.000	0.000
52	Trimethyl-Cyclopentane	0.000	0.000	0.000
53	Dimethyl-Cyclohexane	0.000	0.000	0.000
54	Dimethyl-Cyclohexane	0.000	0.000	0.000
55	Dimethyl-Cyclohexane	.072	0.000	.041
56	2,4 Dimethyl-Hexane	.033	0.000	.019
57	Methyl,Ethyl-Cyclopentane	0.000	0.000	0.000
58	Methyl,Ethyl-Cyclopentane	0.000	0.000	0.000
59	Dimethyl-Cyclohexane	0.000	.395	.170
60	Dimethyl-Cyclohexane	.013	.287	.131
61	Dimethyl-Cyclohexane	.046	1.402	.629
62	C8 Cycloolefin(?)	0.000	.223	.096
63	Methyl-,Ethyl-Cyclopentane	0.000	.567	.244
64	Dimethyl-Cyclohexane	0.000	.194	.084
65	Ethyl-Cyclohexane	.163	.847	.457
66	C8 Cycloolefin(?)	0.000	0.000	0.000
67	C8 Cycloolefin(?)	0.000	0.000	0.000
68	C8 Cycloolefin(?)	0.000	0.000	0.000
69	Ethyl-Benzene	.169	0.000	.096
70	p- & m-Xylenes	9.006	1.028	5.576
71	Unknown	0.000	0.000	0.000
72	o-Xylene	2.780	.243	1.689
73	Unknown	.009	0.000	.005
74	Unknown	0.000	0.000	0.000
75	Unknown	0.000	0.000	0.000
76	Unknown	0.000	0.000	0.000
77	Propyl-Benzene	0.000	0.000	0.000
78	Methyl-,Ethyl-Benzene	.586	0.000	.334
79	Methyl-,Ethyl-Benzene	.275	0.000	.157
80	Trimethyl-Benzene	6.769	.305	3.989
81	Methyl-,Ethyl-Benzene	.144	0.000	.082
82	Trimethyl-Benzene	25.683	1.495	15.282
83	Unknown	0.000	0.000	0.000
84	Trimethyl-Benzene	2.374	.442	1.543
85	Indane	0.000	.376	.162
86	Indene	0.000	0.000	0.000
87	Diethyl-Benzene	.134	1.144	.568
88	Methyl-,Propyl-Benzene	.054	0.000	.031
89	Diethyl-Benzene	.023	0.000	.013
90	Dimethyl-,Ethyl-Benzene	.752	0.000	.429
91	Methyl,-Propyl-Benzene	0.000	0.000	0.000
92	Dimethyl-,Ethyl-Benzene	0.000	0.000	0.000
93	Methyl-Indane	.796	0.000	.454
94	Dimethyl-,Ethyl-Benzene	.778	0.000	.443
95	Dimethyl-,Ethyl-Benzene	.029	0.000	.017
96	Dimethyl-,Ethyl-Benzene	.111	0.000	.063
97	Tetramethyl-Benzene	12.100	0.000	6.897
98	Tetramethyl-Benzene	12.107	0.000	6.901
99	Methyl-Indane	.790	0.000	.450
100	Methyl-Indane	.302	0.000	.172
101	Tetramethyl-Benzene	3.048	0.000	1.738
102	Tetraline	0.000	0.000	0.000
103	Dimethyl-,n-Propyl-Benzene	0.000	0.000	0.000
104	Dimethyl-,n-Propyl-Benzene	.058	0.000	.033
105	Dimethyl-,n-Propyl-Benzene	.059	0.000	.034
106	Dimethyl-Indane	.041	0.000	.024
107	Dimethyl-Indane	.232	0.000	.133

108	Dimethyl-Indane	.275	0.000	.157
109	Trimethyl-,Ethyl-Benzene	.543	0.000	.310
110	Trimethyl-,Ethyl-Benzene	.687	0.000	.392
111	Dimethyl-,Isopropyl-Benzene	.014	0.000	.008
112	Dimethyl-Tetralin	.242	0.000	.138
113	Dimethyl-,Isopropyl-Benzene(?)	.045	0.000	.026
114	Dimethyl-Tetralin	.033	0.000	.019
115	Dimethyl-Tetralin	.110	0.000	.063
116	Dimethyl-Indane	.061	0.000	.035
117	Dimethyl-Indane	.037	0.000	.021
118	Dimethyl-Indane	2.254	0.000	1.285
119	Pentamethyl-Benzene	2.274	0.000	1.296
120	Methyl-Naphtalene	1.520	0.000	.866
121	Methyl-Naphtalene	.617	0.000	.352
122	Dimethyl-Tetralin	.209	0.000	.119
123	Trimethyl-Indane	.085	0.000	.048
124	Trimethyl-Tetralin	.056	0.000	.032
125	Trimethyl-,Isopropyl-Benzene	.148	0.000	.084
126	Tetramethyl-Indane	.115	0.000	.065
127	Dimethyl-Tetralin	.674	0.000	.384
128	Dimethyl-Naphtalene	1.466	0.000	.836
129	Dimethyl-Naphtalene	1.687	0.000	.961
130	Dimethyl-Naphtalene	.081	0.000	.046
131	C12H30	.319	0.000	.182
132	Hexamethyl-Benzene	.361	0.000	.206
133	Trimethyl-Tetralin	.055	0.000	.032
134	Isopropyl-Naphtalene	.092	0.000	.052
135	Isopropyl-Naphtalene	.352	0.000	.201
136	Trimethyl-Naphtalene	.459	0.000	.262
137	Trimethyl-Naphtalene	.448	0.000	.255
138	Trimethyl-Naphtalene	.269	0.000	.153
139	Trimethyl-Naphtalene	.389	0.000	.222
140	Trimethyl-Naphtalene	.443	0.000	.252
141	Trimethyl-Naphtalene	.061	0.000	.035
142	Methyl-,Propyl-Naphtalene	.033	0.000	.019
143	Methyl-,Isopropyl-Naphtalene	.096	0.000	.054
144	Methyl-,Isopropyl-Naphtalene	.054	0.000	.031
145	Methyl-,Isopropyl-Naphtalene	.130	0.000	.074
146	Methyl-,Isopropyl-Naphtalene	.033	0.000	.019
147	Methyl-,Propyl-Naphtalene	.051	0.000	.029
148	Methyl-,Propyl-Naphtalene	.195	0.000	.111
149	Methyl-,Propyl-Naphtalene	.262	0.000	.149
150	C15H18 Naphtalene	.406	0.000	.231
151	C15H18 Naphtalene	.086	0.000	.049
152	C15H18 Naphtalene	.192	0.000	.110
153	C15h18 Naphtalene	.167	0.000	.095
154	C15h18 Naphtalene	.063	0.000	.036
155	Dimethyl-,Isopropyl-Naphtalene	.069	0.000	.040
156	Dimethyl-,Isopropyl-Naphtalene	.024	0.000	.014
157	Dimethyl-,Isopropyl-Naphtalene	.055	0.000	.032
158	Dimethyl-,Isopropyl-Naphtalene	.059	0.000	.034
159	Dimethyl-,Isopropyl-Naphtalene	.654	0.000	.373

```
     *****LUMPED LIQUID & TOTAL C5+ HYDROCARBON    MASS DISTRIBUTIONS*****

COMPOUND                                    LIQUID              TOTAL


n-Pentane                                   0.00                 .42
i-Pentane                                   0.00                2.41
Pentenes                                    0.00                0.00
Cyclopentane                                0.00                0.00
n-Hexane                                    0.00                0.00
Methyl-Pentanes                             0.00                 .34
Dimethyl-Butane                             0.00                 .15
Hexenes                                     0.00                0.00
Cyclohexane                                 0.00                0.00
Methyl-Cyclopentane                         0.00                 .07
Methyl-Cyclopentenes                        0.00                0.00
n-Heptane                                   0.00                0.00
C7 branched Paraffins                       0.00                0.00
C7 unsaturated chains                       0.00                0.00
C7 branched Cycloparaffins                   .08                 .14
C7 branched Cycloolefins                    0.00                0.00
n-Octane                                    0.00                0.00
C8 branched Paraffins                        .04                 .04
C8 unsaturated chains                       0.00                0.00
C8 branched Cycloparaffins                   .31                2.78
C8 branched Cycloolefins                    0.00                 .15
C9+ P+O+N                                    .01                 .01
Benzene                                      .05                 .20
Toluene                                     1.19                1.43
Ethyl-Benzene                                .17                 .15
m-& p-Xylenes                               9.01                8.80
o-Xylene                                    2.78                2.67
Trimethyl-Benzenes                         34.83               32.85
Methyl-,Ethyl-Benzenes                      1.00                 .90
C3-Benzenes                                 0.00                0.00
Diethyl-Benzenes                             .16                 .92
C3-,Methyl-Benzenes                          .05                 .05
Dimethyl-,Ethyl-Benzenes                    1.67                1.50
Tetramethyl-Benzenes                       27.26               24.52
Indane                                      0.00                 .25
Indene                                      0.00                0.00
Methyl-Indane                               1.89                1.70
Tetralin                                    0.00                0.00
C11 alkyl-Benzenes                          3.68                3.31
Dimethyl-Indanes                            2.90                2.61
Methyl-Naphtalene                           2.14                1.92
C12 alkyl-Benzenes                           .51                 .46
C12 alkyl-Indanes                            .08                 .08
C12 alkyl-Tetralins                         1.27                1.14
C12 alkyl-Naphtalenes                       3.23                2.91
C13 alkyl-Indanes                            .11                 .10
C13 alkyl-Tetralins                          .11                 .10
C13 alkyl-Naphtalenes                       2.51                2.26
C14 alkyl-Naphtalenes                        .85                 .77
C15 alkyl-Naphtalenes                       1.78                1.60
```

```
 *****SUMMARY TABLE OF LIQUID & TOTAL C5+    HYDROCARBON COMPOSITIONS*****

COMPOUND                                          LIQUID             TOTAL


C5-C8 Paraffins + Cycloparaffins                    .44               6.35
C5-C8 Olefins + Cycloolefins                       0.00                .15
C9+ P+O+N                                           .01                .01
Benzene                                             .05                .20
Toluene                                            1.19               1.43
C8 Aromatics                                      11.95              11.62
C9 Aromatics                                      35.83              34.01
C10 Aromatics                                     31.02              28.69
C11 Aromatics                                      8.72               7.85
C12 Aromatics                                      5.10               4.58
C13 Aromatics                                      2.74               2.46
C14 Aromatics                                       .85                .77
C15 Aromatics                                      1.78               1.60

          *****LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION*****

COMPOUND                                   WEIGHT % OF TOTAL HYDROCARBONS


Methane                                                 2.77
Ethylene                                                 .27
Ethane                                                 14.69
Propylene                                                .09
Propane                                                13.55
i-Butane                                                2.95
n-Butane                                                2.24
Butenes                                                  .07

C5+ HYDROCARBONS

Paraffins + Cycloparaffins                              4.03
Olefins + Cycloolefins                                   .10
Aromatics                                              48.12
C11+                                                   10.94
```

Appendix I

Mass balance results (PO reactor).

```
              ****************************************
              *                                      *
              *     SYNTHESIS GAS CONVERSION RUN     *
              *                                      *
              *               P0880201               *
              *                                      *
              ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 358.2  C
         PRESSURE:  34 atm
         GAS FLOW: 16.80 l/min
   RESIDENCE TIME:  36.1 s
      H2/CO ratio: 1.05
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 175 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 20.6 %
  H2 CONVERSION:  7.8 %

****************************
    PRODUCT DISTRIBUTION
****************************

             MASS OF GASOLINE:    38.55 g

        MASS OF AQUEOUS PHASE:     2.88 g
            COMPOSITION (WT%):    99.81 % WATER
                                    .19 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2      76.68
             H2O       1.62
             HC       21.70
             METOH      .00

***********************
     MASS BALANCE
***********************

                    IN (g)        OUT (g)        %ERROR

     CARBON:       711.57         695.38          2.28
   HYDROGEN:       124.38         125.25          -.70
     OXYGEN:       948.76         941.81           .73

      TOTAL:      1784.71        1762.43          1.25
```

```
                    ***************************************
                    *                                     *
                    *     SYNTHESIS GAS CONVERSION RUN    *
                    *                                     *
                    *              PO880203               *
                    *                                     *
                    ***************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 372.2  C
         PRESSURE:  34 atm
         GAS FLOW:  3.27 l/min
   RESIDENCE TIME: 181.4 s
     H2/CO ratio:  .96
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 195 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 50.3 %
  H2 CONVERSION: 36.1 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:     31.53 g

         MASS OF AQUEOUS PHASE:     0.00 g
             COMPOSITION (WT%):     0.00 % WATER
                                    0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

            CO2      72.38
            H2O        .45
            HC       27.18
            METOH     0.00

***********************
     MASS BALANCE
***********************

                 IN (g)        OUT (g)        %ERROR

     CARBON:     161.48        167.34          -3.63
   HYDROGEN:      25.79         23.50           8.88
     OXYGEN:     215.31        213.27            .95

      TOTAL:     402.57        404.10          -.38
```

```
                  ****************************************
                  *                                      *
                  *     SYNTHESIS GAS CONVERSION RUN     *
                  *                                      *
                  *              PO880204                *
                  *                                      *
                  ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 353.7  C
         PRESSURE:  34 atm
         GAS FLOW:  3.24 l/min
   RESIDENCE TIME: 188.5 s
     H2/CO ratio:   .96
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 225 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 33.1 %
  H2 CONVERSION: 21.6 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:    23.11 g

       MASS OF AQUEOUS PHASE:     0.00 g
           COMPOSITION (WT%):     0.00 % WATER
                                  0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2     77.94
             H2O       .32
             HC      21.74
             METOH    0.00

***********************
     MASS BALANCE
***********************

                    IN (g)        OUT (g)       %ERROR

      CARBON:      184.09         184.18          -.05
    HYDROGEN:       29.57          27.32          7.60
      OXYGEN:      245.45         250.49         -2.05

       TOTAL:      459.11         461.99          -.63
```

```
                    ******************************************
                    *                                        *
                    *     SYNTHESIS GAS CONVERSION RUN       *
                    *                                        *
                    *               PO880208                 *
                    *                                        *
                    ******************************************

******************************
    OPERATING CONDITIONS
******************************

      TEMPERATURE: 368.7  C
         PRESSURE:  34 atm
         GAS FLOW:  5.84 l/min
   RESIDENCE TIME: 102.1 s
      H2/CO ratio: 1.06
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 185 minutes

*********************
    CONVERSIONS
*********************

  CO CONVERSION: 30.5 %
  H2 CONVERSION: 21.2 %

******************************
    PRODUCT DISTRIBUTION
******************************

             MASS OF GASOLINE:    29.60 g

         MASS OF AQUEOUS PHASE:    0.00 g
             COMPOSITION (WT%):    0.00 % WATER
                                   0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

              CO2      76.06
              H2O        .27
              HC       23.68
              METOH     0.00

************************
     MASS BALANCE
************************

                      IN (g)        OUT (g)       %ERROR

        CARBON:      260.53        266.94         -2.46
      HYDROGEN:       45.87         42.73          6.84
        OXYGEN:      347.37        356.99         -2.77

         TOTAL:      653.77        666.66         -1.97
```

```
                  *******************************************
                  *                                         *
                  *      SYNTHESIS GAS CONVERSION RUN       *
                  *                                         *
                  *                P0880210                 *
                  *                                         *
                  *******************************************

******************************
    OPERATING CONDITIONS
******************************

      TEMPERATURE: 370.9  C
         PRESSURE:  20 atm
         GAS FLOW:  2.35 l/min
   RESIDENCE TIME: 151.8 s
     H2/CO ratio:   .96
    COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 185 minutes

*********************
    CONVERSIONS
*********************

  CO CONVERSION: 36.2 %
  H2 CONVERSION: 24.2 %

******************************
    PRODUCT DISTRIBUTION
******************************

             MASS OF GASOLINE:    10.86 g

        MASS OF AQUEOUS PHASE:     0.00 g
            COMPOSITION (WT%):     0.00 % WATER
                                   0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

              CO2      77.55
              H2O        .26
              HC       22.19
              METOH     0.00

************************
     MASS BALANCE
************************

                      IN (g)       OUT (g)       %ERROR

        CARBON:      110.08       106.61          3.15
      HYDROGEN:       17.58        16.15          8.17
        OXYGEN:      146.78       144.83          1.32

         TOTAL:      274.44       267.60          2.49
```

```
               ****************************************
               *                                      *
               *     SYNTHESIS GAS CONVERSION RUN     *
               *                                      *
               *               PO880212               *
               *                                      *
               ****************************************

****************************
    OPERATING CONDITIONS
****************************

     TEMPERATURE: 371.3  C
        PRESSURE:  34 atm
        GAS FLOW:  3.27 l/min
  RESIDENCE TIME: 181.7 s
    H2/CO ratio:   .96
    COOLANT FLOW:  8.2 kg/hr
   TEST DURATION: 260 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 41.2 %
  H2 CONVERSION: 26.4 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:     30.76 g

       MASS OF AQUEOUS PHASE:      0.00 g
           COMPOSITION (WT%):      0.00 % WATER
                                   0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2      75.63
             H2O       1.42
             HC       22.95
             METOH     0.00

***********************
     MASS BALANCE
***********************

                  IN (g)       OUT (g)       %ERROR

       CARBON:    215.31       221.73         -2.98
     HYDROGEN:     34.38        32.97          4.11
       OXYGEN:    287.07       301.03         -4.86

        TOTAL:    536.76       555.73         -3.53
```

```
               ****************************************
               *                                      *
               *     SYNTHESIS GAS CONVERSION RUN     *
               *                                      *
               *              P0880225                *
               *                                      *
               ****************************************

 *****************************
     OPERATING CONDITIONS
 *****************************

       TEMPERATURE: 376.3  C
          PRESSURE:  34 atm
          GAS FLOW: 16.70 l/min
    RESIDENCE TIME:  35.3 s
       H2/CO ratio: 1.04
     COOLANT FLOW:  8.2 kg/hr
     TEST DURATION: 200 minutes

 ********************
     CONVERSIONS
 ********************

   CO CONVERSION: 24.1 %
   H2 CONVERSION:  9.4 %

 *****************************
     PRODUCT DISTRIBUTION
 *****************************

             MASS OF GASOLINE:    39.84 g

        MASS OF AQUEOUS PHASE:     6.78 g
            COMPOSITION (WT%):    99.74 % WATER
                                    .26 % METHANOL

   PRODUCT MASS DISTRIBUTION (WT%):

              CO2      73.28
              H2O       2.25
              HC       24.47
              METOH      .00

 ***********************
      MASS BALANCE
 ***********************

                    IN (g)        OUT (g)        %ERROR

        CARBON:     813.22        787.17          3.20
      HYDROGEN:     140.50        143.17         -1.91
        OXYGEN:    1084.30       1052.89          2.90

         TOTAL:    2038.02       1983.23          2.69
```

```
                  ****************************************
                  *                                      *
                  *     SYNTHESIS GAS CONVERSION RUN     *
                  *                                      *
                  *              P0880302                *
                  *                                      *
                  ****************************************

****************************
   OPERATING CONDITIONS
****************************

      TEMPERATURE: 375.5  C
         PRESSURE:  34 atm
         GAS FLOW: 16.10 l/min
   RESIDENCE TIME:  36.7 s
     H2/CO ratio: 1.04
    COOLANT FLOW:  8.2 kg/hr
   TEST DURATION: 195 minutes

********************
   CONVERSIONS
********************

  CO CONVERSION: 21.6 %
  H2 CONVERSION:  5.8 %

****************************
   PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:     45.70 g

       MASS OF AQUEOUS PHASE:      5.79 g
           COMPOSITION (WT%):     99.49 % WATER
                                    .51 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2      71.57
             H2O       3.17
             HC       25.25
             METOH      .01

***********************
    MASS BALANCE
***********************

                   IN (g)        OUT (g)        %ERROR

     CARBON:      763.88         770.80          -.91
   HYDROGEN:      132.15         141.17         -6.83
     OXYGEN:     1018.51        1027.82          -.91

      TOTAL:     1914.55        1939.79         -1.32
```

```
                    ****************************************
                    *                                      *
                    *     SYNTHESIS GAS CONVERSION RUN     *
                    *                                      *
                    *              P0880304                *
                    *                                      *
                    ****************************************

*****************************
    OPERATING CONDITIONS
*****************************

      TEMPERATURE: 365.4  C
         PRESSURE:  34 atm
         GAS FLOW: 16.90 l/min
   RESIDENCE TIME:  35.5 s
     H2/CO ratio: 1.41
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 200 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 20.9 %
  H2 CONVERSION:  3.6 %

*****************************
    PRODUCT DISTRIBUTION
*****************************

               MASS OF GASOLINE:    27.76 g

         MASS OF AQUEOUS PHASE:     8.93 g
             COMPOSITION (WT%):    99.51 % WATER
                                     .49 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

               CO2       71.29
               H2O        4.24
               HC        24.45
               METOH       .01

***********************
     MASS BALANCE
***********************

                     IN (g)        OUT (g)        %ERROR

         CARBON:     694.21        674.43           2.85
       HYDROGEN:     163.64        169.98          -3.88
         OXYGEN:     925.62        904.52           2.28

          TOTAL:    1783.47       1748.93           1.94
```

```
                  ****************************************
                  *                                      *
                  *    SYNTHESIS GAS CONVERSION RUN      *
                  *                                      *
                  *              P0880307                *
                  *                                      *
                  ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 365.9  C
         PRESSURE:  34 atm
         GAS FLOW: 15.70 l/min
   RESIDENCE TIME:  38.2 s
     H2/CO ratio:   .73
    COOLANT FLOW:  8.2 kg/hr
   TEST DURATION: 175 minutes

********************
    CONVERSIONS
********************

   CO CONVERSION: 18.1 %
   H2 CONVERSION:  4.3 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:     29.87 g

       MASS OF AQUEOUS PHASE:     0.00 g
           COMPOSITION (WT%):     0.00 % WATER
                                  0.00 % METHANOL

   PRODUCT MASS DISTRIBUTION (WT%):

               CO2      75.17
               H2O        .97
               HC       23.87
               METOH     0.00

***********************
     MASS BALANCE
***********************

                    IN (g)       OUT (g)       %ERROR

        CARBON:     789.67       755.23          4.36
      HYDROGEN:      95.45       100.25         -5.02
        OXYGEN:    1052.89      1008.89          4.18

         TOTAL:    1938.02      1864.37          3.80
```

```
                   ****************************************
                   *                                      *
                   *     SYNTHESIS GAS CONVERSION RUN     *
                   *                                      *
                   *              PO880308                *
                   *                                      *
                   ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 369.8  C
         PRESSURE:  34 atm
         GAS FLOW:  3.19 l/min
   RESIDENCE TIME: 186.7 s
      H2/CO ratio:  .96
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 190 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 38.5 %
  H2 CONVERSION: 24.5 %

****************************
    PRODUCT DISTRIBUTION
****************************

              MASS OF GASOLINE:    21.80 g

       MASS OF AQUEOUS PHASE:       0.00 g
           COMPOSITION (WT%):       0.00 % WATER
                                    0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

               CO2      76.01
               H2O        .33
               HC       23.66
               METOH     0.00

***********************
     MASS BALANCE
***********************

                       IN (g)       OUT (g)       %ERROR

        CARBON:      153.57       163.45         -6.43
      HYDROGEN:       24.50        23.91          2.39
        OXYGEN:      204.76       219.01         -6.96

         TOTAL:      382.83       406.37         -6.15
```

```
                    ****************************************
                    *                                      *
                    *      SYNTHESIS GAS CONVERSION RUN    *
                    *                                      *
                    *              P0880309                *
                    *                                      *
                    ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 349.9  C
         PRESSURE:  34 atm
         GAS FLOW: 16.80 l/min
   RESIDENCE TIME:  36.6 s
     H2/CO ratio: 1.05
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 170 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 18.6 %
  H2 CONVERSION:  2.0 %

****************************
    PRODUCT DISTRIBUTION
****************************

           MASS OF GASOLINE:    17.01 g

      MASS OF AQUEOUS PHASE:     0.00 g
          COMPOSITION (WT%):     0.00 % WATER
                                 0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2       74.22
             H2O        2.49
             HC        23.29
             METOH      0.00

***********************
     MASS BALANCE
***********************

                   IN (g)        OUT (g)        %ERROR

     CARBON:       691.24        629.27           8.97
   HYDROGEN:       120.83        123.99          -2.62
     OXYGEN:       921.65        842.82           8.55

      TOTAL:      1733.72       1596.08           7.94
```

```
                    ******************************************
                    *                                        *
                    *     SYNTHESIS GAS CONVERSION RUN       *
                    *                                        *
                    *               P0880314                 *
                    *                                        *
                    ******************************************

 ******************************
     OPERATING CONDITIONS
 ******************************

       TEMPERATURE: 368.5  C
          PRESSURE:  34 atm
          GAS FLOW: 16.70 l/min
    RESIDENCE TIME:  35.7 s
       H2/CO ratio:   .99
      COOLANT FLOW: 16.6 kg/hr
     TEST DURATION: 155 minutes

 *********************
     CONVERSIONS
 *********************

   CO CONVERSION: 20.3 %
   H2 CONVERSION:  1.0 %

 ******************************
     PRODUCT DISTRIBUTION
 ******************************

            MASS OF GASOLINE:    22.03 g

      MASS OF AQUEOUS PHASE:     2.80 g
          COMPOSITION (WT%):    99.58 % WATER
                                  .42 % METHANOL

   PRODUCT MASS DISTRIBUTION (WT%):

             CO2      72.62
             H2O       1.94
             HC       25.44
             METOH      .01

 ************************
     MASS BALANCE
 ************************

                     IN (g)        OUT (g)       %ERROR

       CARBON:      645.62        610.30          5.47
     HYDROGEN:      106.32        114.17         -7.38
       OXYGEN:      860.83        811.69          5.71

        TOTAL:     1612.77       1536.17          4.75
```

```
                  ****************************************
                  *                                      *
                  *     SYNTHESIS GAS CONVERSION RUN     *
                  *                                      *
                  *              P0880316                *
                  *                                      *
                  ****************************************

*****************************
   OPERATING CONDITIONS
*****************************

      TEMPERATURE: 381.8  C
         PRESSURE:  34 atm
         GAS FLOW:  3.36 l/min
   RESIDENCE TIME: 174.0 s
     H2/CO ratio:   .79
    COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 185 minutes

********************
   CONVERSIONS
********************

  CO CONVERSION: 48.2 %
  H2 CONVERSION: 24.3 %

*****************************
   PRODUCT DISTRIBUTION
*****************************

            MASS OF GASOLINE:    23.33 g

       MASS OF AQUEOUS PHASE:     0.00 g
           COMPOSITION (WT%):     0.00 % WATER
                                  0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

               CO2      76.44
               H2O        .20
               HC       23.36
               METOH     0.00

***********************
     MASS BALANCE
***********************

                    IN (g)        OUT (g)        %ERROR

        CARBON:     172.46        162.47           5.79
      HYDROGEN:      22.63         22.94          -1.38
        OXYGEN:     229.95        218.68           4.90

         TOTAL:     425.04        404.09           4.93
```

```
                    ****************************************
                    *                                      *
                    *     SYNTHESIS GAS CONVERSION RUN     *
                    *                                      *
                    *              P0880317                *
                    *                                      *
                    ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 381.4  C
         PRESSURE:  34 atm
         GAS FLOW:  6.02 l/min
   RESIDENCE TIME:  97.2 s
      H2/CO ratio:  .89
     COOLANT FLOW:  8.2 kg/hr
    TEST DURATION: 200 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 34.9 %
  H2 CONVERSION: 15.6 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:   20.84 g

       MASS OF AQUEOUS PHASE:    1.84 g
           COMPOSITION (WT%):  100.00 % WATER
                                 0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

            CO2      77.45
            H2O        .97
            HC       21.58
            METOH     0.00

***********************
     MASS BALANCE
***********************

                     IN (g)       OUT (g)       %ERROR

       CARBON:      315.37        307.96          2.35
     HYDROGEN:       46.94         48.46         -3.23
       OXYGEN:      420.50        422.67          -.52

        TOTAL:      782.81        779.09           .48
```

```
                    ****************************************
                    *                                      *
                    *     SYNTHESIS GAS CONVERSION RUN     *
                    *                                      *
                    *              P0880318                *
                    *                                      *
                    ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 366.9  C
         PRESSURE:  20 atm
         GAS FLOW: 10.90 l/min
   RESIDENCE TIME:  32.9 s
     H2/CO ratio:   .95
    COOLANT FLOW:  8.2 kg/hr
   TEST DURATION: 165 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 16.4 %
  H2 CONVERSION:  3.3 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:      9.57 g

       MASS OF AQUEOUS PHASE:      0.00 g
           COMPOSITION (WT%):      0.00 % WATER
                                   0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2      73.15
             H2O       1.80
             HC       25.05
             METOH     0.00

***********************
     MASS BALANCE
***********************

                      IN (g)       OUT (g)        %ERROR

       CARBON:      458.18       447.71          2.29
     HYDROGEN:       72.27        75.88         -4.99
       OXYGEN:      610.91       596.38          2.38

        TOTAL:     1141.36      1119.97          1.87
```

```
                    ****************************************
                    *                                      *
                    *     SYNTHESIS GAS CONVERSION RUN     *
                    *                                      *
                    *               P0880322               *
                    *                                      *
                    ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 370.0  C
         PRESSURE:  34 atm
         GAS FLOW:  3.31 l/min
   RESIDENCE TIME: 179.8 s
     H2/CO ratio:   .81
    COOLANT FLOW: 16.6 kg/hr
    TEST DURATION: 200 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 39.2 %
  H2 CONVERSION: 19.9 %

****************************
    PRODUCT DISTRIBUTION
****************************

           MASS OF GASOLINE:    26.44 g

      MASS OF AQUEOUS PHASE:     0.00 g
          COMPOSITION (WT%):     0.00 % WATER
                                 0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

              CO2      71.56
              H2O       2.47
              HC       25.97
              METOH     0.00

***********************
     MASS BALANCE
***********************

                     IN (g)       OUT (g)       %ERROR

      CARBON:       181.49       176.53          2.73
    HYDROGEN:        24.46        25.30         -3.41
      OXYGEN:       241.98       232.32          3.99

       TOTAL:       447.93       434.15          3.08
```

```
              ****************************************
              *                                      *
              *     SYNTHESIS GAS CONVERSION RUN     *
              *                                      *
              *               PO880323               *
              *                                      *
              ****************************************

****************************
    OPERATING CONDITIONS
****************************

      TEMPERATURE: 355.5  C
         PRESSURE:  34 atm
         GAS FLOW:  6.16 l/min
   RESIDENCE TIME:  98.9 s
     H2/CO ratio:   .88
     COOLANT FLOW: 16.6 kg/hr
    TEST DURATION: 180 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 22.7 %
  H2 CONVERSION:  1.3 %

****************************
    PRODUCT DISTRIBUTION
****************************

            MASS OF GASOLINE:     13.46 g

       MASS OF AQUEOUS PHASE:      1.24 g
           COMPOSITION (WT%):    100.00 % WATER
                                   0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

             CO2      78.54
             H2O       2.05
             HC       19.41
             METOH     0.00

***********************
     MASS BALANCE
***********************

                    IN (g)       OUT (g)       %ERROR

      CARBON:       292.76       277.10          5.35
    HYDROGEN:        42.84        46.10         -7.59
      OXYGEN:       390.35       380.12          2.62

       TOTAL:       725.95       703.32          3.12
```

```
                    ******************************************
                    *                                        *
                    *      SYNTHESIS GAS CONVERSION RUN      *
                    *                                        *
                    *               PO880325                 *
                    *                                        *
                    ******************************************

*****************************
    OPERATING CONDITIONS
*****************************

      TEMPERATURE: 369.9  C
         PRESSURE:  34 atm
         GAS FLOW:  3.33 l/min
   RESIDENCE TIME: 178.8 s
     H2/CO ratio:   .96
    COOLANT FLOW:   8.2 kg/hr
    TEST DURATION: 170 minutes

********************
    CONVERSIONS
********************

  CO CONVERSION: 33.3 %
  H2 CONVERSION: 26.0 %

*****************************
    PRODUCT DISTRIBUTION
*****************************

            MASS OF GASOLINE:    21.75 g

       MASS OF AQUEOUS PHASE:     0.00 g
           COMPOSITION (WT%):     0.00 % WATER
                                  0.00 % METHANOL

  PRODUCT MASS DISTRIBUTION (WT%):

              CO2       73.43
              H2O        1.02
              HC        25.55
              METOH      0.00

***********************
     MASS BALANCE
***********************

                      IN (g)        OUT (g)       %ERROR

       CARBON:       143.31        153.75          -7.29
     HYDROGEN:        22.90         21.75           5.01
       OXYGEN:       191.07        202.29          -5.87

        TOTAL:       357.28        377.79          -5.74
```

Appendix J

Temperature profile calculation (PO reactor).

```
                ****************************************
                *                                      *
                *          TEMPERATURE PROFILE         *
                *             RUN P0880201             *
                *                                      *
                ****************************************


              TEMPERATURE READINGS BEFORE REACTANTS FEEDING
              ---------------------------------------------

                           ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)

   LEVEL   1         0.006       367.3       366.5       366.9
   LEVEL   2         0.156       368.6       367.9       366.6
   LEVEL   3         0.356       368.6       367.1       366.9
   LEVEL   4         0.556       365.8       366.2       365.7
   LEVEL   5         0.756       366.5       366.8       364.6
   LEVEL   6         0.956       367.7       367.6       366.0
   LEVEL   7         1.156       368.8       368.0       365.9
   LEVEL   8         1.356       367.6       365.5       365.3
   LEVEL   9         1.556       365.0       364.1       362.9
   LEVEL  10         1.706       366.8       365.3       365.5


                            ** COOLANT SIDE **

                      x (m)      TC (C)

   LEVEL   1         0.056       366.8
   LEVEL   2         0.456       361.5
   LEVEL   3         0.856       362.6
   LEVEL   4         1.256       365.6
   LEVEL   5         1.656       366.0

   INITIAL MEAN TEMPERATURE: 366.47
   INITIAL COOLANT TEMPERATURE: 364.50


                TEMPERATURE READINGS DURING THE REACTION
                ----------------------------------------

                            ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

   LEVEL   1         0.006       353.3       358.9       360.8       358.2
   LEVEL   2         0.156       372.9       369.8       363.3       367.9
   LEVEL   3         0.356       377.8       371.3       366.3       370.9
   LEVEL   4         0.556       373.3       369.8       368.1       370.0
   LEVEL   5         0.756       374.1       371.2       369.1       371.1
   LEVEL   6         0.956       376.0       373.9       371.8       373.6
   LEVEL   7         1.156       377.8       376.2       372.9       375.2
   LEVEL   8         1.356       377.6       374.3       373.6       374.9
   LEVEL   9         1.556       375.8       373.9       372.1       373.7
   LEVEL  10         1.706       378.8       375.7       374.9       376.2
```

```
                   ** COOLANT SIDE **

            x (m)       TC (C)

LEVEL   1   0.056       361.8
LEVEL   2   0.456       360.1
LEVEL   3   0.856       368.5
LEVEL   4   1.256       371.6
LEVEL   5   1.656       372.8


      REVISED TEMPERATURE PROFILE FOR THE REACTION
      --------------------------------------------

                   ** REACTOR SIDE **

            x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1   0.006       353.3       358.9       360.8       358.2
LEVEL   2   0.156       371.6       368.4       363.6       367.2
LEVEL   3   0.356       376.5       370.7       366.3       370.4
LEVEL   4   0.556       374.8       370.1       369.3       371.0
LEVEL   5   0.756       374.9       370.9       371.4       372.2
LEVEL   6   0.956       375.6       372.8       372.7       373.5
LEVEL   7   1.156       376.3       374.7       373.9       374.8
LEVEL   8   1.356       377.3       375.3       375.2       375.8
LEVEL   9   1.556       378.1       376.3       376.1       376.7
LEVEL  10   1.706       379.3       376.9       376.3       377.3

                   ** COOLANT SIDE **

            x (m)       TC (C)

LEVEL   1   0.056       361.8
LEVEL   2   0.456       365.4
LEVEL   3   0.856       372.7
LEVEL   4   1.256       372.8
LEVEL   5   1.656       373.6
```

```
                 **************************************
                 *                                    *
                 *         TEMPERATURE PROFILE        *
                 *            RUN P0880204            *
                 *                                    *
                 **************************************


               TEMPERATURE READINGS BEFORE REACTANTS FEEDING
               ---------------------------------------------

                             ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)

      LEVEL   1       0.006      349.2       348.7       348.6
      LEVEL   2       0.156      349.7       349.3       348.3
      LEVEL   3       0.356      349.8       348.5       348.7
      LEVEL   4       0.556      347.6       347.7       347.2
      LEVEL   5       0.756      348.5       348.7       346.7
      LEVEL   6       0.956      350.3       350.0       348.6
      LEVEL   7       1.156      351.9       351.1       349.3
      LEVEL   8       1.356      351.2       349.1       349.0
      LEVEL   9       1.556      348.9       347.9       346.7
      LEVEL  10       1.706      350.6       349.0       349.2

                              ** COOLANT SIDE **

                      x (m)      TC (C)

      LEVEL   1       0.056      349.4
      LEVEL   2       0.456      343.0
      LEVEL   3       0.856      344.1
      LEVEL   4       1.256      348.2
      LEVEL   5       1.656      349.2

      INITIAL MEAN TEMPERATURE: 349.00
      INITIAL COOLANT TEMPERATURE: 346.78


                 TEMPERATURE READINGS DURING THE REACTION
                 ----------------------------------------

                              ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

      LEVEL   1       0.006      359.1       354.0       353.1       355.0
      LEVEL   2       0.156      360.7       357.9       354.3       357.1
      LEVEL   3       0.356      361.4       357.3       355.8       357.8
      LEVEL   4       0.556      357.9       356.3       355.7       356.5
      LEVEL   5       0.756      358.7       357.7       355.8       357.2
      LEVEL   6       0.956      360.5       359.5       358.0       359.1
      LEVEL   7       1.156      362.2       361.0       358.8       360.4
      LEVEL   8       1.356      361.7       359.3       359.1       359.9
      LEVEL   9       1.556      359.1       358.1       357.1       357.9
      LEVEL  10       1.706      361.9       359.5       359.7       360.2
```

```
                          ** COOLANT SIDE **

                    x (m)       TC (C)

LEVEL   1          0.056       353.7
LEVEL   2          0.456       347.8
LEVEL   3          0.856       353.7
LEVEL   4          1.256       357.4
LEVEL   5          1.656       358.4


          REVISED TEMPERATURE PROFILE FOR THE REACTION
          --------------------------------------------

                          ** REACTOR SIDE **

                    x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1          0.006       359.1       354.0       353.1       355.0  416.6
LEVEL   2          0.156       360.2       357.3       354.6       356.9  341.3
LEVEL   3          0.356       360.8       357.5       355.7       357.6  427.7
LEVEL   4          0.556       359.5       357.3       357.1       357.8  542.3
LEVEL   5          0.756       359.4       357.7       357.7       358.2  122.1
LEVEL   6          0.956       359.4       358.2       358.0       358.4  242.[illegible]
LEVEL   7          1.156       359.5       358.6       358.1       358.6  43[illegible]
LEVEL   8          1.356       359.7       358.9       358.7       359.0
LEVEL   9          1.556       359.4       358.9       359.0       359.1
LEVEL  10          1.706       360.5       359.2       359.1       359.5

                          ** COOLANT SIDE **

                    x (m)       TC (C)

LEVEL   1          0.056       353.7
LEVEL   2          0.456       354.2
LEVEL   3          0.856       359.0
LEVEL   4          1.256       358.6
LEVEL   5          1.656       358.6
```

```
          *************************************
          *                                   *
          *        TEMPERATURE PROFILE        *
          *           RUN P0880208            *
          *                                   *
          *************************************


        TEMPERATURE READINGS BEFORE REACTANTS FEEDING
        ---------------------------------------------

                    ** REACTOR SIDE **

                 x (m)      TC (C)      TH (C)      TW (C)

 LEVEL   1       0.006      368.0       368.1       367.9
 LEVEL   2       0.156      367.8       367.3       366.2
 LEVEL   3       0.356      367.8       366.5       366.4
 LEVEL   4       0.556      365.8       366.0       365.3
 LEVEL   5       0.756      366.6       366.6       364.6
 LEVEL   6       0.956      367.5       367.3       365.7
 LEVEL   7       1.156      368.5       367.7       365.7
 LEVEL   8       1.356      367.7       365.7       365.3
 LEVEL   9       1.556      365.6       364.7       363.2
 LEVEL  10       1.706      366.8       365.3       365.7


                    ** COOLANT SIDE **

                 x (m)      TC (C)

 LEVEL   1       0.056      367.6
 LEVEL   2       0.456      361.7
 LEVEL   3       0.856      362.5
 LEVEL   4       1.256      365.2
 LEVEL   5       1.656      365.7

 INITIAL MEAN TEMPERATURE: 366.44
 INITIAL COOLANT TEMPERATURE: 364.54


          TEMPERATURE READINGS DURING THE REACTION
          ----------------------------------------

                    ** REACTOR SIDE **

                 x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

 LEVEL   1       0.006      376.0       369.7       368.4       370.8
 LEVEL   2       0.156      381.9       376.6       369.6       375.1
 LEVEL   3       0.356      379.5       374.1       371.3       374.4
 LEVEL   4       0.556      374.7       372.3       371.6       372.7
 LEVEL   5       0.756      375.1       373.3       371.4       373.0
 LEVEL   6       0.956      376.3       374.7       372.9       374.4
 LEVEL   7       1.156      377.3       375.8       373.4       375.2
 LEVEL   8       1.356      377.1       374.1       373.6       374.7
 LEVEL   9       1.556      374.2       373.1       371.9       372.9
 LEVEL  10       1.706      377.2       374.1       374.2       375.0
```

```
                        ** COOLANT SIDE **

                 x (m)        TC (C)

LEVEL    1      0.056         368.7
LEVEL    2      0.456         364.4
LEVEL    3      0.856         368.7
LEVEL    4      1.256         371.9
LEVEL    5      1.656         373.8


          REVISED TEMPERATURE PROFILE FOR THE REACTION
          --------------------------------------------

                       ** REACTOR SIDE **

                 x (m)        TC (C)        TH (C)        TW (C)        TAV (C)

LEVEL    1      0.006         376.0         369.7         368.4         370.8
LEVEL    2      0.156         382.1         377.4         371.3         376.1
LEVEL    3      0.356         379.7         375.7         372.8         375.6
LEVEL    4      0.556         376.9         374.4         374.2         375.0
LEVEL    5      0.756         376.5         374.8         374.7         375.2
LEVEL    6      0.956         376.6         375.5         375.1         375.7
LEVEL    7      1.156         376.8         376.2         375.6         376.1
LEVEL    8      1.356         377.4         376.5         376.2         376.6
LEVEL    9      1.556         376.6         376.5         376.6         376.6
LEVEL   10      1.706         378.4         376.9         376.4         377.1

                       ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL    1       0.056         368.7
LEVEL    2       0.456         370.3
LEVEL    3       0.856         373.8
LEVEL    4       1.256         374.3
LEVEL    5       1.656         375.7
```

```
*************************************
*                                   *
*       TEMPERATURE PROFILE         *
*          RUN P0880210             *
*                                   *
*************************************


      TEMPERATURE READINGS BEFORE REACTANTS FEEDING
      ---------------------------------------------

                   ** REACTOR SIDE **

              x (m)      TC (C)      TH (C)      TW (C)

LEVEL   1     0.006      368.4       367.9       367.8
LEVEL   2     0.156      369.4       368.9       367.6
LEVEL   3     0.356      369.6       368.0       367.8
LEVEL   4     0.556      367.2       367.2       366.6
LEVEL   5     0.756      368.2       368.2       366.0
LEVEL   6     0.956      369.6       369.2       367.6
LEVEL   7     1.156      370.9       369.8       367.9
LEVEL   8     1.356      369.8       367.6       367.3
LEVEL   9     1.556      367.1       366.2       364.9
LEVEL   10    1.706      368.8       367.1       367.3

                   ** COOLANT SIDE **

              x (m)      TC (C)

LEVEL   1     0.056      368.4
LEVEL   2     0.456      362.3
LEVEL   3     0.856      363.8
LEVEL   4     1.256      367.2
LEVEL   5     1.656      366.8

INITIAL MEAN TEMPERATURE: 368.00
INITIAL COOLANT TEMPERATURE: 365.70

         TEMPERATURE READINGS DURING THE REACTION
         ----------------------------------------

                   ** REACTOR SIDE **

              x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1     0.006      375.2       370.6       370.1       371.6
LEVEL   2     0.156      376.4       373.4       370.4       372.9
LEVEL   3     0.356      376.3       372.8       371.6       373.2
LEVEL   4     0.556      372.7       371.8       371.1       371.7
LEVEL   5     0.756      373.6       372.7       370.8       372.1
LEVEL   6     0.956      374.8       374.1       372.6       373.7
LEVEL   7     1.156      376.2       375.2       373.1       374.6
LEVEL   8     1.356      375.5       373.3       372.9       373.7
LEVEL   9     1.556      372.7       371.6       370.9       371.6
LEVEL   10    1.706      374.9       372.8       373.3       373.6
```

```
                        ** COOLANT SIDE **

                    x (m)      TC (C)

LEVEL    1          0.056      370.9
LEVEL    2          0.456      366.1
LEVEL    3          0.856      367.9
LEVEL    4          1.256      372.1
LEVEL    5          1.656      372.3



              REVISED TEMPERATURE PROFILE FOR THE REACTION
              ----------------------------------------------

                        ** REACTOR SIDE **

                    x (m)      TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1          0.006      375.2        370.6        370.1        371.6
LEVEL    2          0.156      375.4        372.4        370.6        372.4
LEVEL    3          0.356      375.1        372.7        371.6        372.9
LEVEL    4          0.556      373.9        372.5        372.3        372.8
LEVEL    5          0.756      373.8        372.4        372.6        372.9
LEVEL    6          0.956      373.6        372.8        372.8        373.0
LEVEL    7          1.156      373.7        373.3        373.0        373.3
LEVEL    8          1.356      374.1        373.6        373.4        373.7
LEVEL    9          1.556      374.0        373.3        373.8        373.7
LEVEL    10         1.706      374.5        373.6        373.8        373.9

                        ** COOLANT SIDE **

                     x (m)      TC (C)

LEVEL    1           0.056      370.9
LEVEL    2           0.456      372.2
LEVEL    3           0.856      372.5
LEVEL    4           1.256      373.3
LEVEL    5           1.656      373.9
```

```
                 ***************************************
                 *                                     *
                 *         TEMPERATURE PROFILE         *
                 *            RUN P0880212             *
                 *                                     *
                 ***************************************


             TEMPERATURE READINGS BEFORE REACTANTS FEEDING
             ---------------------------------------------

                          ** REACTOR SIDE **

                    x (m)      TC (C)      TH (C)      TW (C)

     LEVEL   1      0.006      367.2       367.6       367.7
     LEVEL   2      0.156      368.7       368.2       366.8
     LEVEL   3      0.356      368.9       367.3       367.1
     LEVEL   4      0.556      366.4       366.3       365.8
     LEVEL   5      0.756      367.1       367.2       365.1
     LEVEL   6      0.956      368.2       367.9       366.3
     LEVEL   7      1.156      369.3       368.4       366.2
     LEVEL   8      1.356      368.3       366.1       365.8
     LEVEL   9      1.556      365.4       364.1       363.1
     LEVEL  10      1.706      367.0       365.5       365.6


                          ** COOLANT SIDE **

                    x (m)      TC (C)

     LEVEL   1      0.056      368.1
     LEVEL   2      0.456      361.4
     LEVEL   3      0.856      363.3
     LEVEL   4      1.256      365.8
     LEVEL   5      1.656      364.4

     INITIAL MEAN TEMPERATURE: 366.82
     INITIAL COOLANT TEMPERATURE: 364.60


               TEMPERATURE READINGS DURING THE REACTION
               ----------------------------------------

                          ** REACTOR SIDE **

                    x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

     LEVEL   1      0.006      379.5       371.5       370.6       373.3
     LEVEL   2      0.156      380.9       376.1       371.4       375.4
     LEVEL   3      0.356      379.8       374.8       373.0       375.4
     LEVEL   4      0.556      375.3       373.7       372.8       373.8
     LEVEL   5      0.756      376.2       374.8       372.7       374.3
     LEVEL   6      0.956      377.4       376.1       374.5       375.8
     LEVEL   7      1.156      378.9       377.6       375.2       376.9
     LEVEL   8      1.356      378.2       375.6       375.1       376.1
     LEVEL   9      1.556      375.2       374.0       373.1       373.9
     LEVEL  10      1.706      377.9       375.4       375.5       376.1
```

```
                        ** COOLANT SIDE **

                  x (m)      TC (C)

LEVEL    1       0.056       371.3
LEVEL    2       0.456       365.3
LEVEL    3       0.856       369.9
LEVEL    4       1.256       373.9
LEVEL    5       1.656       374.1


         REVISED TEMPERATURE PROFILE FOR THE REACTION
         --------------------------------------------

                       ** REACTOR SIDE **

                  x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL    1       0.006       379.5       371.5       370.6       373.3
LEVEL    2       0.156       379.4       375.5       372.3       375.2
LEVEL    3       0.356       378.1       375.1       373.6       375.3
LEVEL    4       0.556       376.1       375.0       374.7       375.2
LEVEL    5       0.756       376.3       375.2       375.3       375.5
LEVEL    6       0.956       376.4       375.8       375.9       376.0
LEVEL    7       1.156       376.8       376.8       376.7       376.8
LEVEL    8       1.356       377.1       377.1       377.0       377.1
LEVEL    9       1.556       377.0       377.5       377.7       377.5
LEVEL    10      1.706       378.1       377.5       377.6       377.7

                       ** COOLANT SIDE **

                  x (m)      TC (C)

LEVEL    1       0.056       371.3
LEVEL    2       0.456       372.0
LEVEL    3       0.856       374.7
LEVEL    4       1.256       376.2
LEVEL    5       1.656       377.8
```

```
                  ****************************************
                  *                                      *
                  *          TEMPERATURE PROFILE         *
                  *             RUN P0880225             *
                  *                                      *
                  ****************************************


                TEMPERATURE READINGS BEFORE REACTANTS FEEDING
                ---------------------------------------------

                              ** REACTOR SIDE **

                      x (m)       TC (C)       TH (C)       TW (C)

      LEVEL   1      0.006        370.4        375.6        376.4
      LEVEL   2      0.156        375.9        375.8        374.7
      LEVEL   3      0.356        376.6        374.9        374.8
      LEVEL   4      0.556        374.5        374.6        373.9
      LEVEL   5      0.756        375.3        375.6        373.3
      LEVEL   6      0.956        376.8        376.5        374.8
      LEVEL   7      1.156        378.1        377.0        375.0
      LEVEL   8      1.356        377.0        375.2        374.5
      LEVEL   9      1.556        374.9        373.7        372.3
      LEVEL   10     1.706        376.7        374.9        375.0

                              ** COOLANT SIDE **

                      x (m)       TC (C)

      LEVEL   1      0.056        376.7
      LEVEL   2      0.456        368.7
      LEVEL   3      0.856        371.1
      LEVEL   4      1.256        374.9
      LEVEL   5      1.656        374.7

      INITIAL MEAN TEMPERATURE: 375.16
      INITIAL COOLANT TEMPERATURE: 373.22


                  TEMPERATURE READINGS DURING THE REACTION
                  ----------------------------------------

                              ** REACTOR SIDE **

                      x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

      LEVEL   1      0.006        373.7        377.2        377.3        376.3
      LEVEL   2      0.156        393.3        390.3        380.2        386.8
      LEVEL   3      0.356        394.9        390.2        383.8        388.8
      LEVEL   4      0.556        391.1        387.2        385.3        387.4
      LEVEL   5      0.756        391.8        388.2        385.7        388.1
      LEVEL   6      0.956        392.8        390.7        388.3        390.3
      LEVEL   7      1.156        395.2        392.9        389.5        392.1
      LEVEL   8      1.356        394.7        391.0        389.6        391.4
      LEVEL   9      1.556        391.4        389.6        387.9        389.4
      LEVEL   10     1.706        394.1        391.1        390.5        391.7
```

```
                        ** COOLANT SIDE **

                x (m)        TC (C)

LEVEL    1      0.056        377.8
LEVEL    2      0.456        379.9
LEVEL    3      0.856        383.0
LEVEL    4      1.256        387.7
LEVEL    5      1.656        389.0


           REVISED TEMPERATURE PROFILE FOR THE REACTION
           --------------------------------------------

                        ** REACTOR SIDE **

                x (m)        TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1      0.006        373.7        377.2        377.3        376.3
LEVEL    2      0.156        387.8        390.1        381.9        386.0
LEVEL    3      0.356        388.7        390.9        385.4        388.0
LEVEL    4      0.556        387.0        388.2        387.8        387.7
LEVEL    5      0.756        386.9        388.2        388.8        388.1
LEVEL    6      0.956        386.4        389.8        389.9        388.9
LEVEL    7      1.156        387.5        391.5        390.9        390.2
LEVEL    8      1.356        388.1        391.4        391.5        390.6
LEVEL    9      1.556        386.9        391.5        392.0        390.5
LEVEL    10     1.706        387.8        391.8        391.9        390.8

                        ** COOLANT SIDE **

                x (m)        TC (C)

LEVEL    1      0.056        377.8
LEVEL    2      0.456        387.9
LEVEL    3      0.856        388.6
LEVEL    4      1.256        389.5
LEVEL    5      1.656        391.0
```

```
                 **************************************
                 *                                    *
                 *          TEMPERATURE PROFILE       *
                 *             RUN P0880302           *
                 *                                    *
                 **************************************


               TEMPERATURE READINGS BEFORE REACTANTS FEEDING
               ---------------------------------------------

                            ** REACTOR SIDE **

                      x (m)       TC (C)       TH (C)       TW (C)

      LEVEL    1     0.006        377.5        377.1        377.7
      LEVEL    2     0.156        377.9        377.6        376.6
      LEVEL    3     0.356        377.7        376.2        376.7
      LEVEL    4     0.556        374.5        374.8        374.6
      LEVEL    5     0.756        374.9        375.4        373.2
      LEVEL    6     0.956        376.1        375.9        374.3
      LEVEL    7     1.156        377.2        376.2        374.4
      LEVEL    8     1.356        376.1        374.2        373.4
      LEVEL    9     1.556        373.2        372.5        370.6
      LEVEL   10     1.706        375.0        373.3        373.6

                            ** COOLANT SIDE **

                      x (m)       TC (C)

      LEVEL    1     0.056        377.8
      LEVEL    2     0.456        371.1
      LEVEL    3     0.856        370.9
      LEVEL    4     1.256        373.8
      LEVEL    5     1.656        372.9

      INITIAL MEAN TEMPERATURE: 375.28
      INITIAL COOLANT TEMPERATURE: 373.30


                 TEMPERATURE READINGS DURING THE REACTION
                 ----------------------------------------

                            ** REACTOR SIDE **

                      x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

      LEVEL    1     0.006        373.0        376.1        376.6        375.5
      LEVEL    2     0.156        391.1        386.6        378.6        384.4
      LEVEL    3     0.356        392.4        387.8        381.8        386.5
      LEVEL    4     0.556        389.6        385.4        383.2        385.6
      LEVEL    5     0.756        389.6        386.3        383.9        386.2
      LEVEL    6     0.956        390.3        388.8        386.3        388.1
      LEVEL    7     1.156        392.6        390.5        387.2        389.7
      LEVEL    8     1.356        392.1        388.5        387.3        389.0
      LEVEL    9     1.556        389.1        387.4        385.7        387.1
      LEVEL   10     1.706        391.8        388.8        388.4        389.4
```

```
                         ** COOLANT SIDE **

                   x (m)       TC (C)

LEVEL    1        0.056        377.3
LEVEL    2        0.456        375.4
LEVEL    3        0.856        382.2
LEVEL    4        1.256        385.8
LEVEL    5        1.656        386.9


            REVISED TEMPERATURE PROFILE FOR THE REACTION
            --------------------------------------------

                        ** REACTOR SIDE **

                   x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1        0.006        373.0        376.1        376.6        375.5
LEVEL    2        0.156        390.7        386.1        379.7        384.6
LEVEL    3        0.356        392.2        388.7        382.8        387.1
LEVEL    4        0.556        392.6        387.7        386.3        388.4
LEVEL    5        0.756        392.2        388.0        388.4        389.3
LEVEL    6        0.956        391.7        390.0        389.7        390.3
LEVEL    7        1.156        392.9        391.4        390.5        391.4
LEVEL    8        1.356        393.5        391.4        391.6        392.1
LEVEL    9        1.556        393.4        392.0        392.8        392.7
LEVEL    10       1.706        394.3        392.6        392.5        393.0

                        ** COOLANT SIDE **

                    x (m)       TC (C)

LEVEL    1         0.056        377.3
LEVEL    2         0.456        382.1
LEVEL    3         0.856        389.1
LEVEL    4         1.256        389.8
LEVEL    5         1.656        391.8
```

```
            ************************************
            *                                  *
            *        TEMPERATURE PROFILE       *
            *           RUN P0880304           *
            *                                  *
            ************************************


          TEMPERATURE READINGS BEFORE REACTANTS FEEDING
          ---------------------------------------------

                      ** REACTOR SIDE **

               x (m)      TC (C)     TH (C)     TW (C)

LEVEL   1     0.006       366.1      365.7      366.2
LEVEL   2     0.156       366.8      366.2      365.3
LEVEL   3     0.356       367.1      365.4      365.5
LEVEL   4     0.556       364.4      364.8      364.1
LEVEL   5     0.756       365.3      365.6      363.3
LEVEL   6     0.956       366.6      366.4      364.9
LEVEL   7     1.156       367.9      367.0      365.2
LEVEL   8     1.356       366.6      364.8      364.2
LEVEL   9     1.556       364.1      363.2      361.5
LEVEL   10    1.706       365.6      363.9      364.1

                      ** COOLANT SIDE **

               x (m)      TC (C)

LEVEL   1     0.056       366.4
LEVEL   2     0.456       357.0
LEVEL   3     0.856       362.2
LEVEL   4     1.256       364.6
LEVEL   5     1.656       363.8

INITIAL MEAN TEMPERATURE: 365.26
INITIAL COOLANT TEMPERATURE: 362.80


            TEMPERATURE READINGS DURING THE REACTION
            ----------------------------------------

                      ** REACTOR SIDE **

               x (m)      TC (C)     TH (C)     TW (C)     TAV (C)

LEVEL   1     0.006       362.5      366.2      366.6      365.4
LEVEL   2     0.156       378.4      374.9      368.9      373.3
LEVEL   3     0.356       379.6      376.1      371.8      375.2
LEVEL   4     0.556       377.2      374.2      372.8      374.4
LEVEL   5     0.756       377.6      375.2      372.9      374.9
LEVEL   6     0.956       378.5      377.5      375.3      376.8
LEVEL   7     1.156       380.9      379.1      376.4      378.4
LEVEL   8     1.356       380.4      377.8      376.6      378.0
LEVEL   9     1.556       377.9      376.3      375.1      376.2
LEVEL   10    1.706       380.3      377.7      377.4      378.3
```

```
                              ** COOLANT SIDE **

                        x (m)      TC (C)

    LEVEL    1        0.056        367.3
    LEVEL    2        0.456        367.1
    LEVEL    3        0.856        371.6
    LEVEL    4        1.256        374.6
    LEVEL    5        1.656        376.4



               REVISED TEMPERATURE PROFILE FOR THE REACTION
               -------------------------------------------

                             ** REACTOR SIDE **

                        x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

    LEVEL    1        0.006        362.5        366.2        366.6        365.4
    LEVEL    2        0.156        377.7        374.4        369.8        373.3
    LEVEL    3        0.356        378.6        376.4        372.5        375.3
    LEVEL    4        0.556        378.9        375.1        374.9        376.0
    LEVEL    5        0.756        378.4        375.3        375.8        376.3
    LEVEL    6        0.956        378.0        376.8        376.6        377.0
    LEVEL    7        1.156        379.1        377.8        377.4        378.0
    LEVEL    8        1.356        379.9        378.7        378.6        379.0
    LEVEL    9        1.556        379.9        378.8        379.8        379.5
    LEVEL    10       1.706        380.8        379.5        379.5        379.9

                             ** COOLANT SIDE **

                         x (m)      TC (C)

    LEVEL    1         0.056        367.3
    LEVEL    2         0.456        376.5
    LEVEL    3         0.856        375.8
    LEVEL    4         1.256        376.4
    LEVEL    5         1.656        379.0
```

```
                 ****************************************
                 *                                      *
                 *          TEMPERATURE PROFILE         *
                 *             RUN P0880307             *
                 *                                      *
                 ****************************************


               TEMPERATURE READINGS BEFORE REACTANTS FEEDING
               ---------------------------------------------

                            ** REACTOR SIDE **

                       x (m)      TC (C)      TH (C)      TW (C)

    LEVEL    1        0.006       367.3       366.6       367.0
    LEVEL    2        0.156       367.9       367.5       366.4
    LEVEL    3        0.356       368.1       366.6       366.7
    LEVEL    4        0.556       365.4       365.7       365.2
    LEVEL    5        0.756       366.2       366.3       364.1
    LEVEL    6        0.956       367.6       367.3       365.7
    LEVEL    7        1.156       368.7       367.9       366.0
    LEVEL    8        1.356       367.6       366.0       365.2
    LEVEL    9        1.556       365.0       364.0       362.4
    LEVEL    10       1.706       366.3       364.8       365.0


                            ** COOLANT SIDE **

                       x (m)      TC (C)

    LEVEL    1        0.056       367.2
    LEVEL    2        0.456       359.7
    LEVEL    3        0.856       363.0
    LEVEL    4        1.256       365.5
    LEVEL    5        1.656       364.0

    INITIAL MEAN TEMPERATURE: 366.22
    INITIAL COOLANT TEMPERATURE: 363.88


                 TEMPERATURE READINGS DURING THE REACTION
                 ----------------------------------------

                            ** REACTOR SIDE **

                       x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

    LEVEL    1        0.006       362.7       366.7       367.3       365.9
    LEVEL    2        0.156       377.7       374.7       369.2       373.2
    LEVEL    3        0.356       380.1       375.8       371.4       375.1
    LEVEL    4        0.556       377.6       374.3       372.4       374.4
    LEVEL    5        0.756       377.9       375.2       372.9       375.0
    LEVEL    6        0.956       378.9       377.7       375.3       377.0
    LEVEL    7        1.156       380.9       379.3       376.6       378.6
    LEVEL    8        1.356       380.4       377.6       376.6       377.9
    LEVEL    9        1.556       377.4       376.3       375.0       376.0
    LEVEL    10       1.706       380.4       377.6       377.3       378.2
```

```
                         ** COOLANT SIDE **

                    x (m)      TC (C)

LEVEL   1          0.056       368.2
LEVEL   2          0.456       364.4
LEVEL   3          0.856       370.6
LEVEL   4          1.256       375.2
LEVEL   5          1.656       376.3



            REVISED TEMPERATURE PROFILE FOR THE REACTION
            --------------------------------------------

                         ** REACTOR SIDE **

                    x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1          0.006       362.7       366.7       367.3       365.9
LEVEL   2          0.156       377.1       373.8       369.8       373.0
LEVEL   3          0.356       379.3       375.8       371.7       375.0
LEVEL   4          0.556       379.5       375.2       374.2       375.9
LEVEL   5          0.756       379.0       375.5       375.8       376.6
LEVEL   6          0.956       378.6       377.0       376.6       377.3
LEVEL   7          1.156       379.5       378.0       377.6       378.2
LEVEL   8          1.356       380.1       378.2       378.4       378.8
LEVEL   9          1.556       379.7       378.9       379.6       379.4
LEVEL   10         1.706       381.4       379.4       379.3       379.9

                         ** COOLANT SIDE **

                    x (m)      TC (C)

LEVEL   1          0.056       368.2
LEVEL   2          0.456       371.9
LEVEL   3          0.856       374.8
LEVEL   4          1.256       376.9
LEVEL   5          1.656       379.5
```

```
                    ************************************
                    *                                  *
                    *        TEMPERATURE PROFILE       *
                    *           RUN P0880308           *
                    *                                  *
                    ************************************


                  TEMPERATURE READINGS BEFORE REACTANTS FEEDING
                  ---------------------------------------------

                              ** REACTOR SIDE **

                         x (m)      TC (C)      TH (C)      TW (C)

        LEVEL    1      0.006       367.0       366.8       367.2
        LEVEL    2      0.156       367.5       367.1       366.3
        LEVEL    3      0.356       367.6       366.0       366.3
        LEVEL    4      0.556       364.6       364.9       364.4
        LEVEL    5      0.756       365.2       365.3       363.3
        LEVEL    6      0.956       366.4       366.2       364.7
        LEVEL    7      1.156       367.4       366.6       364.6
        LEVEL    8      1.356       366.1       364.4       363.8
        LEVEL    9      1.556       363.4       362.6       361.2
        LEVEL   10      1.706       364.8       363.2       363.4

                              ** COOLANT SIDE **

                         x (m)      TC (C)

        LEVEL    1      0.056       367.2
        LEVEL    2      0.456       358.8
        LEVEL    3      0.856       362.3
        LEVEL    4      1.256       364.4
        LEVEL    5      1.656       362.6

        INITIAL MEAN TEMPERATURE: 365.28
        INITIAL COOLANT TEMPERATURE: 363.06


                    TEMPERATURE READINGS DURING THE REACTION
                    ----------------------------------------

                              ** REACTOR SIDE **

                         x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

        LEVEL    1      0.006       379.0       370.8       370.1       372.7
        LEVEL    2      0.156       380.4       375.9       371.3       375.2
        LEVEL    3      0.356       378.9       374.8       373.2       375.2
        LEVEL    4      0.556       375.8       373.5       372.7       373.8
        LEVEL    5      0.756       376.2       374.8       372.6       374.2
        LEVEL    6      0.956       377.4       376.4       374.7       376.0
        LEVEL    7      1.156       379.3       377.8       375.6       377.3
        LEVEL    8      1.356       378.7       376.4       375.4       376.6
        LEVEL    9      1.556       375.7       374.6       373.4       374.4
        LEVEL   10      1.706       378.5       376.2       376.2       376.8
```

```
                        ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL    1        0.056        370.3
LEVEL    2        0.456        365.4
LEVEL    3        0.856        371.9
LEVEL    4        1.256        374.2
LEVEL    5        1.656        373.7


             REVISED TEMPERATURE PROFILE FOR THE REACTION
             --------------------------------------------

                        ** REACTOR SIDE **

                  x (m)        TC (C)        TH (C)        TW (C)        TAV (C)

LEVEL    1        0.006        379.0         370.8         370.1         372.7
LEVEL    2        0.156        379.9         375.6         372.2         375.3
LEVEL    3        0.356        378.3         375.6         374.1         375.7
LEVEL    4        0.556        378.2         375.4         375.5         376.2
LEVEL    5        0.756        378.0         376.3         376.5         376.8
LEVEL    6        0.956        378.0         377.0         377.2         377.4
LEVEL    7        1.156        378.9         378.0         378.2         378.3
LEVEL    8        1.356        379.6         378.8         378.8         379.0
LEVEL    9        1.556        379.3         378.8         379.4         379.2
LEVEL    10       1.706        380.7         379.8         380.0         380.1

                        ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL    1        0.056        370.3
LEVEL    2        0.456        373.8
LEVEL    3        0.856        376.8
LEVEL    4        1.256        377.0
LEVEL    5        1.656        378.3
```

```
                 *************************************
                 *                                   *
                 *        TEMPERATURE PROFILE        *
                 *           RUN P0880309            *
                 *                                   *
                 *************************************


               TEMPERATURE READINGS BEFORE REACTANTS FEEDING
               ---------------------------------------------

                          ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)

    LEVEL   1        0.006       348.9       348.5       348.9
    LEVEL   2        0.156       349.6       349.1       348.2
    LEVEL   3        0.356       349.9       348.3       348.6
    LEVEL   4        0.556       347.3       347.6       347.2
    LEVEL   5        0.756       348.2       348.6       346.2
    LEVEL   6        0.956       349.8       349.6       348.0
    LEVEL   7        1.156       350.9       350.1       348.4
    LEVEL   8        1.356       349.7       348.2       347.6
    LEVEL   9        1.556       347.1       346.4       344.9
    LEVEL  10        1.706       348.9       347.2       347.7


                          ** COOLANT SIDE **

                      x (m)      TC (C)

    LEVEL   1        0.056       349.2
    LEVEL   2        0.456       344.9
    LEVEL   3        0.856       344.9
    LEVEL   4        1.256       346.7
    LEVEL   5        1.656       348.1

    INITIAL MEAN TEMPERATURE: 348.32
    INITIAL COOLANT TEMPERATURE: 346.76


                 TEMPERATURE READINGS DURING THE REACTION
                 ----------------------------------------

                          ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

    LEVEL   1        0.006       346.7       350.9       351.1       349.9
    LEVEL   2        0.156       357.2       355.8       352.1       354.6
    LEVEL   3        0.356       358.0       355.6       353.0       355.1
    LEVEL   4        0.556       356.8       354.2       353.2       354.5
    LEVEL   5        0.756       357.4       355.7       353.4       355.2
    LEVEL   6        0.956       358.9       357.9       356.1       357.4
    LEVEL   7        1.156       360.9       359.9       357.1       359.0
    LEVEL   8        1.356       360.8       358.4       357.5       358.7
    LEVEL   9        1.556       358.5       357.3       355.9       357.0
    LEVEL  10        1.706       361.2       358.9       358.4       359.3
```

```
                         ** COOLANT SIDE **

                  x (m)      TC (C)

LEVEL    1       0.056        351.2
LEVEL    2       0.456        347.7
LEVEL    3       0.856        351.9
LEVEL    4       1.256        355.9
LEVEL    5       1.656        357.9


           REVISED TEMPERATURE PROFILE FOR THE REACTION
           --------------------------------------------

                        ** REACTOR SIDE **

                  x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1       0.006        346.7        350.9        351.1        349.9
LEVEL    2       0.156        356.5        355.2        352.8        354.5
LEVEL    3       0.356        357.0        355.8        353.3        355.1
LEVEL    4       0.556        358.4        355.1        354.9        355.9
LEVEL    5       0.756        358.1        355.6        356.1        356.5
LEVEL    6       0.956        358.0        356.8        357.0        357.2
LEVEL    7       1.156        358.9        358.3        357.6        358.2
LEVEL    8       1.356        360.0        358.7        358.8        359.1
LEVEL    9       1.556        360.3        359.4        359.9        359.9
LEVEL   10       1.706        361.2        360.2        359.6        360.2

                        ** COOLANT SIDE **

                   x (m)      TC (C)

LEVEL    1        0.056        351.2
LEVEL    2        0.456        352.0
LEVEL    3        0.856        356.2
LEVEL    4        1.256        358.4
LEVEL    5        1.656        359.0
```

```
                 ***************************************
                 *                                     *
                 *          TEMPERATURE PROFILE        *
                 *             RUN P0880314            *
                 *                                     *
                 ***************************************


               TEMPERATURE READINGS BEFORE REACTANTS FEEDING
               ---------------------------------------------

                          ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)

      LEVEL   1      0.006      368.1       367.5       367.4
      LEVEL   2      0.156      368.3       367.9       366.6
      LEVEL   3      0.356      368.3       367.3       367.3
      LEVEL   4      0.556      366.8       367.5       366.7
      LEVEL   5      0.756      367.7       368.1       366.0
      LEVEL   6      0.956      368.6       368.5       366.9
      LEVEL   7      1.156      369.6       368.5       366.8
      LEVEL   8      1.356      368.8       367.2       366.7
      LEVEL   9      1.556      367.3       366.3       365.1
      LEVEL  10      1.706      368.4       366.9       367.1

                          ** COOLANT SIDE **

                      x (m)      TC (C)

      LEVEL   1      0.056      366.4
      LEVEL   2      0.456      357.0
      LEVEL   3      0.856      362.2
      LEVEL   4      1.256      364.6
      LEVEL   5      1.656      363.8

      INITIAL MEAN TEMPERATURE: 367.47
      INITIAL COOLANT TEMPERATURE: 362.80


                 TEMPERATURE READINGS DURING THE REACTION
                 ----------------------------------------

                          ** REACTOR SIDE **

                      x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

      LEVEL   1      0.006      365.8       369.4       369.6       368.5
      LEVEL   2      0.156      380.7       377.0       370.5       375.2
      LEVEL   3      0.356      380.1       376.0       372.1       375.5
      LEVEL   4      0.556      378.6       373.8       372.4       374.5
      LEVEL   5      0.756      377.1       374.6       372.5       374.4
      LEVEL   6      0.956      377.7       376.1       374.1       375.7
      LEVEL   7      1.156      378.9       377.3       374.3       376.5
      LEVEL   8      1.356      378.5       375.7       374.6       376.0
      LEVEL   9      1.556      376.0       374.6       373.6       374.6
      LEVEL  10      1.706      377.9       375.3       375.2       376.0
```

```
                        ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL   1        0.056        370.8
LEVEL   2        0.456        368.3
LEVEL   3        0.856        370.5
LEVEL   4        1.256        372.7
LEVEL   5        1.656        374.1



          REVISED TEMPERATURE PROFILE FOR THE REACTION
          ---------------------------------------------

                       ** REACTOR SIDE **

                  x (m)        TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL   1        0.006        365.8        369.4        369.6        368.5
LEVEL   2        0.156        380.5        376.6        371.3        375.4
LEVEL   3        0.356        379.9        376.2        372.2        375.5
LEVEL   4        0.556        379.9        373.8        373.1        375.1
LEVEL   5        0.756        377.5        374.0        373.9        374.9
LEVEL   6        0.956        377.2        375.1        374.6        375.5
LEVEL   7        1.156        377.4        376.3        374.9        376.0
LEVEL   8        1.356        377.8        376.0        375.3        376.2
LEVEL   9        1.556        376.8        375.8        375.9        376.1
LEVEL   10       1.706        377.6        375.9        375.5        376.2

                       ** COOLANT SIDE **

                   x (m)        TC (C)

LEVEL   1         0.056        370.8
LEVEL   2         0.456        377.7
LEVEL   3         0.856        374.7
LEVEL   4         1.256        374.5
LEVEL   5         1.656        376.7
```

```
          ****************************************
          *                                      *
          *         TEMPERATURE PROFILE          *
          *            RUN P0880316              *
          *                                      *
          ****************************************


        TEMPERATURE READINGS BEFORE REACTANTS FEEDING
        ---------------------------------------------

                    ** REACTOR SIDE **

                x (m)       TC (C)      TH (C)      TW (C)

LEVEL   1       0.006       378.1       377.7       378.6
LEVEL   2       0.156       378.5       378.1       377.3
LEVEL   3       0.356       378.7       377.1       377.2
LEVEL   4       0.556       376.1       376.2       375.5
LEVEL   5       0.756       376.7       376.8       374.9
LEVEL   6       0.956       378.1       377.8       376.2
LEVEL   7       1.156       379.3       378.4       376.4
LEVEL   8       1.356       378.3       376.5       375.9
LEVEL   9       1.556       375.6       374.8       373.3
LEVEL   10      1.706       378.0       375.9       376.1


                    ** COOLANT SIDE **

                x (m)       TC (C)

LEVEL   1       0.056       378.9
LEVEL   2       0.456       371.9
LEVEL   3       0.856       373.4
LEVEL   4       1.256       375.4
LEVEL   5       1.656       374.9

INITIAL MEAN TEMPERATURE: 376.94
INITIAL COOLANT TEMPERATURE: 374.90


          TEMPERATURE READINGS DURING THE REACTION
          ----------------------------------------

                    ** REACTOR SIDE **

                x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1       0.006       392.8       382.9       382.0       385.2
LEVEL   2       0.156       392.7       387.7       382.9       387.0
LEVEL   3       0.356       391.1       386.0       384.1       386.6
LEVEL   4       0.556       387.4       384.8       383.8       385.1
LEVEL   5       0.756       387.4       385.8       383.5       385.3
LEVEL   6       0.956       388.3       387.1       385.2       386.6
LEVEL   7       1.156       389.8       388.2       385.9       387.7
LEVEL   8       1.356       388.9       386.6       385.6       386.8
LEVEL   9       1.556       385.9       384.7       383.8       384.6
LEVEL   10      1.706       388.2       385.9       385.8       386.5
```

```
                    ** COOLANT SIDE **

                x (m)      TC (C)

LEVEL   1       0.056      382.0
LEVEL   2       0.456      377.5
LEVEL   3       0.856      382.0
LEVEL   4       1.256      384.4
LEVEL   5       1.656      384.8


          REVISED TEMPERATURE PROFILE FOR THE REACTION
          --------------------------------------------

                    ** REACTOR SIDE **

                x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1       0.006      392.8       382.9       382.0       385.2
LEVEL   2       0.156      392.3       387.3       384.2       387.3
LEVEL   3       0.356      390.5       386.6       385.5       387.2
LEVEL   4       0.556      389.4       386.3       386.9       387.4
LEVEL   5       0.756      388.8       386.7       387.2       387.5
LEVEL   6       0.956      388.3       387.0       387.6       387.6
LEVEL   7       1.156      388.6       387.5       388.1       388.1
LEVEL   8       1.356      388.7       387.8       388.3       388.3
LEVEL   9       1.556      388.4       387.6       389.1       388.5
LEVEL   10      1.706      388.3       387.7       388.3       388.1

                    ** COOLANT SIDE **

                x (m)      TC (C)

LEVEL   1       0.056      382.0
LEVEL   2       0.456      384.5
LEVEL   3       0.856      387.5
LEVEL   4       1.256      387.9
LEVEL   5       1.656      388.8
```

```
               ****************************************
               *                                      *
               *          TEMPERATURE PROFILE         *
               *             RUN P0880317             *
               *                                      *
               ****************************************


             TEMPERATURE READINGS BEFORE REACTANTS FEEDING
             ---------------------------------------------

                          ** REACTOR SIDE **

                    x (m)      TC (C)      TH (C)      TW (C)

   LEVEL   1      0.006       378.0       377.7       377.3
   LEVEL   2      0.156       377.9       377.7       376.9
   LEVEL   3      0.356       377.6       376.2       376.9
   LEVEL   4      0.556       374.8       374.8       374.4
   LEVEL   5      0.756       375.2       375.3       373.3
   LEVEL   6      0.956       376.2       376.1       374.5
   LEVEL   7      1.156       377.2       376.3       374.5
   LEVEL   8      1.356       376.1       374.4       373.8
   LEVEL   9      1.556       373.1       372.4       371.6
   LEVEL  10      1.706       374.8       373.3       373.8

                          ** COOLANT SIDE **

                    x (m)      TC (C)

   LEVEL   1      0.056       377.9
   LEVEL   2      0.456       370.3
   LEVEL   3      0.856       371.7
   LEVEL   4      1.256       374.2
   LEVEL   5      1.656       372.9

   INITIAL MEAN TEMPERATURE: 375.40
   INITIAL COOLANT TEMPERATURE: 373.40


               TEMPERATURE READINGS DURING THE REACTION
               ----------------------------------------

                          ** REACTOR SIDE **

                    x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

   LEVEL   1      0.006       391.5       382.6       381.1       384.4
   LEVEL   2      0.156       397.6       390.8       383.2       389.4
   LEVEL   3      0.356       394.3       388.2       385.3       388.6
   LEVEL   4      0.556       390.7       386.2       385.2       387.0
   LEVEL   5      0.756       389.6       387.2       384.9       386.9
   LEVEL   6      0.956       390.8       389.0       386.9       388.6
   LEVEL   7      1.156       392.1       390.3       387.8       389.7
   LEVEL   8      1.356       391.3       388.6       387.5       388.9
   LEVEL   9      1.556       387.8       386.6       385.7       386.5
   LEVEL  10      1.706       390.9       387.6       387.9       388.6
```

```
                      ** COOLANT SIDE **

                  x (m)       TC (C)

LEVEL    1       0.056       381.5
LEVEL    2       0.456       380.6
LEVEL    3       0.856       383.4
LEVEL    4       1.256       386.4
LEVEL    5       1.656       386.4


            REVISED TEMPERATURE PROFILE FOR THE REACTION
            --------------------------------------------

                      ** REACTOR SIDE **

                  x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1       0.006       391.5        382.6        381.1        384.4
LEVEL    2       0.156       397.7        390.8        383.6        389.6
LEVEL    3       0.356       394.7        389.7        385.7        389.4
LEVEL    4       0.556       393.9        389.1        388.1        390.0
LEVEL    5       0.756       392.4        389.6        388.9        390.1
LEVEL    6       0.956       392.6        390.6        389.7        390.8
LEVEL    7       1.156       392.9        391.7        390.6        391.6
LEVEL    8       1.356       393.2        391.9        391.0        391.9
LEVEL    9       1.556       392.7        391.9        391.4        391.9
LEVEL    10      1.706       394.1        392.0        391.4        392.3

                      ** COOLANT SIDE **

                   x (m)       TC (C)

LEVEL    1        0.056       381.5
LEVEL    2        0.456       388.2
LEVEL    3        0.856       389.6
LEVEL    4        1.256       390.1
LEVEL    5        1.656       391.4
```

```
              ****************************************
              *                                      *
              *          TEMPERATURE PROFILE         *
              *             RUN P0880318             *
              *                                      *
              ****************************************


            TEMPERATURE READINGS BEFORE REACTANTS FEEDING
            ---------------------------------------------

                         ** REACTOR SIDE **

                  x (m)       TC (C)      TH (C)      TW (C)

LEVEL   1        0.006        368.0       367.3       367.7
LEVEL   2        0.156        368.3       367.9       366.9
LEVEL   3        0.356        368.5       367.0       367.2
LEVEL   4        0.556        366.1       366.2       365.5
LEVEL   5        0.756        366.9       367.0       364.8
LEVEL   6        0.956        368.3       368.1       366.3
LEVEL   7        1.156        369.6       368.7       366.6
LEVEL   8        1.356        368.4       366.8       366.1
LEVEL   9        1.556        365.8       365.2       363.9
LEVEL  10        1.706        367.9       366.2       366.3

                         ** COOLANT SIDE **

                  x (m)       TC (C)

LEVEL   1        0.056        368.1
LEVEL   2        0.456        362.9
LEVEL   3        0.856        363.9
LEVEL   4        1.256        365.5
LEVEL   5        1.656        366.7

INITIAL MEAN TEMPERATURE: 366.98
INITIAL COOLANT TEMPERATURE: 365.42


              TEMPERATURE READINGS DURING THE REACTION
              ----------------------------------------

                         ** REACTOR SIDE **

                  x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL   1        0.006        364.8       367.5       367.8       366.9
LEVEL   2        0.156        376.5       373.7       369.5       372.7
LEVEL   3        0.356        376.7       372.8       370.9       373.0
LEVEL   4        0.556        374.5       371.6       370.6       372.0
LEVEL   5        0.756        374.3       372.8       370.8       372.4
LEVEL   6        0.956        375.4       374.5       372.6       373.9
LEVEL   7        1.156        377.1       376.1       373.4       375.2
LEVEL   8        1.356        376.6       374.3       373.4       374.5
LEVEL   9        1.556        373.7       372.6       371.9       372.6
LEVEL  10        1.706        376.8       374.0       374.2       374.8
```

```
                       ** COOLANT SIDE **

                   x (m)      TC (C)

LEVEL    1        0.056       369.4
LEVEL    2        0.456       364.6
LEVEL    3        0.856       368.8
LEVEL    4        1.256       372.0
LEVEL    5        1.656       372.3



           REVISED TEMPERATURE PROFILE FOR THE REACTION
           --------------------------------------------

                      ** REACTOR SIDE **

                   x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

LEVEL    1        0.006       364.8       367.5       367.8       366.9
LEVEL    2        0.156       376.2       373.1       370.3       372.8
LEVEL    3        0.356       376.2       373.1       371.4       373.2
LEVEL    4        0.556       376.4       372.7       372.8       373.7
LEVEL    5        0.756       375.4       373.1       373.7       374.0
LEVEL    6        0.956       375.1       373.7       374.0       374.2
LEVEL    7        1.156       375.5       374.7       374.5       374.8
LEVEL    8        1.356       376.2       374.8       375.0       375.3
LEVEL    9        1.556       375.9       374.7       375.7       375.4
LEVEL    10       1.706       376.9       375.1       375.6       375.8

                      ** COOLANT SIDE **

                    x (m)      TC (C)

LEVEL    1         0.056       369.4
LEVEL    2         0.456       369.8
LEVEL    3         0.856       373.0
LEVEL    4         1.256       374.6
LEVEL    5         1.656       373.7
```

```
                  ***************************************
                  *                                     *
                  *         TEMPERATURE PROFILE         *
                  *            RUN P0880322             *
                  *                                     *
                  ***************************************


                TEMPERATURE READINGS BEFORE REACTANTS FEEDING
                ---------------------------------------------

                            ** REACTOR SIDE **

                     x (m)       TC (C)      TH (C)      TW (C)

     LEVEL    1      0.006       366.2       366.2       366.3
     LEVEL    2      0.156       366.7       366.3       365.4
     LEVEL    3      0.356       367.0       365.6       365.8
     LEVEL    4      0.556       365.6       365.7       364.9
     LEVEL    5      0.756       366.7       366.6       364.6
     LEVEL    6      0.956       367.5       367.2       365.5
     LEVEL    7      1.156       368.2       367.4       365.6
     LEVEL    8      1.356       367.2       365.6       365.4
     LEVEL    9      1.556       365.4       364.6       363.4
     LEVEL    10     1.706       366.5       365.0       365.2


                            ** COOLANT SIDE **

                     x (m)       TC (C)

     LEVEL    1      0.056       367.2
     LEVEL    2      0.456       362.2
     LEVEL    3      0.856       363.3
     LEVEL    4      1.256       365.7
     LEVEL    5      1.656       363.8

     INITIAL MEAN TEMPERATURE: 365.98
     INITIAL COOLANT TEMPERATURE: 364.44


                  TEMPERATURE READINGS DURING THE REACTION
                  ----------------------------------------

                            ** REACTOR SIDE **

                     x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

     LEVEL    1      0.006       377.6       371.1       370.0       372.4
     LEVEL    2      0.156       378.2       374.2       370.2       373.6
     LEVEL    3      0.356       377.2       372.5       371.2       373.2
     LEVEL    4      0.556       374.2       371.8       371.0       372.1
     LEVEL    5      0.756       374.3       372.7       370.9       372.4
     LEVEL    6      0.956       374.9       374.0       372.2       373.5
     LEVEL    7      1.156       375.7       374.5       372.4       373.9
     LEVEL    8      1.356       375.1       373.2       372.4       373.4
     LEVEL    9      1.556       372.7       371.8       371.1       371.7
     LEVEL    10     1.706       374.6       372.5       372.8       373.2
```

```
                         ** COOLANT SIDE **

                     x (m)       TC (C)

    LEVEL    1      0.056        370.6
    LEVEL    2      0.456        368.3
    LEVEL    3      0.856        370.4
    LEVEL    4      1.256        371.9
    LEVEL    5      1.656        372.1


             REVISED TEMPERATURE PROFILE FOR THE REACTION
             --------------------------------------------

                         ** REACTOR SIDE **

                     x (m)       TC (C)      TH (C)      TW (C)      TAV (C)

    LEVEL    1      0.006        377.6       371.1       370.0       372.4
    LEVEL    2      0.156        377.7       374.1       371.1       373.8
    LEVEL    3      0.356        376.4       373.1       371.7       373.4
    LEVEL    4      0.556        374.8       372.3       372.4       373.0
    LEVEL    5      0.756        373.8       372.3       372.6       372.8
    LEVEL    6      0.956        373.6       373.0       373.0       373.2
    LEVEL    7      1.156        373.7       373.3       373.1       373.3
    LEVEL    8      1.356        374.1       373.8       373.3       373.7
    LEVEL    9      1.556        373.5       373.4       374.0       373.7
    LEVEL    10     1.706        374.3       373.7       373.9       373.9

                         ** COOLANT SIDE **

                     x (m)       TC (C)

    LEVEL    1      0.056        370.6
    LEVEL    2      0.456        373.3
    LEVEL    3      0.856        374.3
    LEVEL    4      1.256        373.4
    LEVEL    5      1.656        375.5
```

```
                    ***************************************
                    *                                     *
                    *          TEMPERATURE PROFILE        *
                    *             RUN P0880323            *
                    *                                     *
                    ***************************************


                  TEMPERATURE READINGS BEFORE REACTANTS FEEDING
                  ---------------------------------------------

                              ** REACTOR SIDE **

                         x (m)      TC (C)      TH (C)      TW (C)

        LEVEL   1        0.006      350.0       350.3       349.7
        LEVEL   2        0.156      350.5       350.4       349.5
        LEVEL   3        0.356      350.7       349.4       349.9
        LEVEL   4        0.556      348.9       349.7       348.9
        LEVEL   5        0.756      349.8       350.1       348.2
        LEVEL   6        0.956      350.8       350.6       349.1
        LEVEL   7        1.156      351.8       350.8       349.2
        LEVEL   8        1.356      351.0       349.1       348.8
        LEVEL   9        1.556      349.1       348.5       347.5
        LEVEL  10        1.706      350.4       348.9       348.9


                              ** COOLANT SIDE **

                         x (m)      TC (C)

        LEVEL   1        0.056      350.9
        LEVEL   2        0.456      344.3
        LEVEL   3        0.856      346.9
        LEVEL   4        1.256      349.0
        LEVEL   5        1.656      347.8

        INITIAL MEAN TEMPERATURE: 349.68
        INITIAL COOLANT TEMPERATURE: 347.78


                    TEMPERATURE READINGS DURING THE REACTION
                    ----------------------------------------

                              ** REACTOR SIDE **

                         x (m)      TC (C)      TH (C)      TW (C)      TAV (C)

        LEVEL   1        0.006      358.5       356.3       354.4       356.1
        LEVEL   2        0.156      362.4       359.5       355.3       358.5
        LEVEL   3        0.356      362.0       357.9       356.4       358.4
        LEVEL   4        0.556      359.4       357.0       356.2       357.3
        LEVEL   5        0.756      359.3       357.9       356.3       357.6
        LEVEL   6        0.956      359.8       358.9       357.1       358.4
        LEVEL   7        1.156      360.8       359.7       357.3       359.0
        LEVEL   8        1.356      360.2       358.3       357.8       358.6
        LEVEL   9        1.556      358.0       357.1       356.2       357.0
        LEVEL  10        1.706      359.9       357.8       358.2       358.5
```

```
                         ** COOLANT SIDE **

                    x (m)       TC (C)

LEVEL    1          0.056       355.5
LEVEL    2          0.456       352.2
LEVEL    3          0.856       354.9
LEVEL    4          1.256       356.8
LEVEL    5          1.656       357.6


             REVISED TEMPERATURE PROFILE FOR THE REACTION
             --------------------------------------------

                        ** REACTOR SIDE **

                    x (m)       TC (C)       TH (C)       TW (C)       TAV (C)

LEVEL    1          0.006       358.5        356.3        354.4        356.1
LEVEL    2          0.156       361.9        359.4        355.5        358.4
LEVEL    3          0.356       361.3        358.8        356.2        358.4
LEVEL    4          0.556       360.5        357.6        357.0        358.1
LEVEL    5          0.756       359.5        358.1        357.8        358.4
LEVEL    6          0.956       359.0        358.6        357.7        358.3
LEVEL    7          1.156       359.0        359.2        357.8        358.6
LEVEL    8          1.356       359.2        359.5        358.7        359.1
LEVEL    9          1.556       358.9        358.9        358.4        358.7
LEVEL    10         1.706       359.5        359.2        359.0        359.2

                        ** COOLANT SIDE **

                    x (m)       TC (C)

LEVEL    1          0.056       355.5
LEVEL    2          0.456       358.8
LEVEL    3          0.856       358.9
LEVEL    4          1.256       358.7
LEVEL    5          1.656       360.7
```

```
            *****************************************
            *                                       *
            *         TEMPERATURE PROFILE           *
            *            RUN P0880325               *
            *                                       *
            *****************************************


          TEMPERATURE READINGS BEFORE REACTANTS FEEDING
          ---------------------------------------------

                      ** REACTOR SIDE **

                x (m)      TC (C)     TH (C)     TW (C)

LEVEL   1     0.006      366.9      366.7      366.6
LEVEL   2     0.156      367.2      366.8      366.0
LEVEL   3     0.356      367.6      365.9      366.0
LEVEL   4     0.556      365.2      365.2      364.6
LEVEL   5     0.756      365.9      366.0      363.8
LEVEL   6     0.956      367.1      366.8      365.3
LEVEL   7     1.156      368.2      367.3      365.7
LEVEL   8     1.356      367.0      365.4      364.8
LEVEL   9     1.556      364.4      363.7      362.4
LEVEL  10     1.706      366.3      364.4      364.7

                       ** COOLANT SIDE **

                x (m)      TC (C)

LEVEL   1     0.056      367.0
LEVEL   2     0.456      361.2
LEVEL   3     0.856      362.3
LEVEL   4     1.256      364.8
LEVEL   5     1.656      363.5

INITIAL MEAN TEMPERATURE: 365.80
INITIAL COOLANT TEMPERATURE: 363.76


            TEMPERATURE READINGS DURING THE REACTION
            ----------------------------------------

                       ** REACTOR SIDE **

                x (m)      TC (C)     TH (C)     TW (C)     TAV (C)

LEVEL   1     0.006      377.8      370.7      369.4      372.1
LEVEL   2     0.156      379.1      374.8      370.7      374.2
LEVEL   3     0.356      378.6      373.7      372.1      374.3
LEVEL   4     0.556      374.6      372.6      371.8      372.8
LEVEL   5     0.756      375.1      373.8      371.8      373.3
LEVEL   6     0.956      376.1      375.2      373.8      374.9
LEVEL   7     1.156      377.8      376.6      374.5      376.0
LEVEL   8     1.356      377.1      375.0      374.5      375.4
LEVEL   9     1.556      374.2      373.3      372.3      373.1
LEVEL  10     1.706      377.2      374.8      374.9      375.5
```

```
                         ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL    1       0.056         369.9
LEVEL    2       0.456         365.2
LEVEL    3       0.856         369.7
LEVEL    4       1.256         373.2
LEVEL    5       1.656         373.2


             REVISED TEMPERATURE PROFILE FOR THE REACTION
             --------------------------------------------

                        ** REACTOR SIDE **

                  x (m)        TC (C)        TH (C)        TW (C)        TAV (C)

LEVEL    1       0.006         377.8         370.7         369.4         372.1
LEVEL    2       0.156         378.8         374.7         371.3         374.4
LEVEL    3       0.356         377.9         374.5         372.7         374.7
LEVEL    4       0.556         376.3         374.1         373.8         374.6
LEVEL    5       0.756         376.1         374.5         374.6         375.0
LEVEL    6       0.956         375.9         375.1         375.1         375.3
LEVEL    7       1.156         376.5         376.0         375.4         375.9
LEVEL    8       1.356         377.0         376.3         376.3         376.5
LEVEL    9       1.556         376.7         376.3         376.5         376.5
LEVEL   10       1.706         377.8         377.1         376.8         377.2

                        ** COOLANT SIDE **

                  x (m)        TC (C)

LEVEL    1       0.056         369.9
LEVEL    2       0.456         371.0
LEVEL    3       0.856         374.4
LEVEL    4       1.256         375.4
LEVEL    5       1.656         376.7
```

Appendix K

Simulation equations and assumptions (PO reactor).

The model used in the simulation is the basic pseudohomogeneous one-dimensional model. Mass and energy conservation equations may be written as follows (a nomenclature is presented at the end of this appendix):

$$-\frac{dp}{dz} = A\ p\ \exp(-a/T + b)$$

$$-\frac{dT}{dz} = B\ p\ \exp(-a/T + b) - C\ (T - Tc)$$

$$-\frac{dTc}{dz} = D\ (T - Tc)$$

with: $A = P\ M\ \rho_B/(u_s\ \rho_g)$; $B = (-\Delta H)\ \rho_B/(u_s\ Cp_g\ \rho_g)$;

$C = 2\ U/(u_s\ Cp_s\ \rho_g\ R)$; $D = 2\ \pi\ R\ t_n\ U/(W_c\ Cp_c)$

The overall heat transfer coefficient can be evaluated with the following equation (Froment (1962)):

$$\frac{1}{U} = \frac{1}{h_{out}} + \frac{1}{\alpha_w} + \frac{R}{4k_{er}}$$

with:

$$h_{out} = kc\ /\ 0.0015\ /\ (0.203\ Re_c^{0.33}\ Pr_c^{0.33} + 0.22\ Re_c^{0.8} Pr_c^{0.4})$$

$$\alpha_w = \frac{k_g}{d_p} \exp(0.077 + 0.523\ \ln Re_p)$$

$$k_{er} = k_g\ (8.33 + Pr\ Re_p\ 1/Pe_{mr})$$

$$Pe_{mr} = u_s\ d_p/D_{er}$$

$$D_{er} = (u_s\ d_p)\ /\ (10\ (1 + 19.4\ (d_p/2R)^2\ )$$

The assumptions that have to be made for using a one-dimensional model are the following:

a) Mass and thermal axial dispersion effects are neglected.

b) Partial pressure and temperature gradients between the solid catalyst and the gaseous reacting stream are neglected.

c) The axial pressure drop throughout the bed is comparatively small with respect to the total pressure.

d) The overall heat transfer coefficient, U, is considered constant.

e) Temperature and partial pressure are constant in the cross section of the reactor.

Reactor Characteristics

- Particle diameter: 2.8 mm
- Reactor lenght: 2 m
- Catalytic bed lenght: 1.856 m
- Number of tubes: 1
- External tube diameter: 3.51 cm
- Internal tube diameter: 2.66 cm

Reactant and coolant properties

Heat capacity of the gas mixture estimated in Kcal/kg°C with the following equation:

$$Cp = \Sigma Cp_i (p_i/P)$$

Thermal conductivity of the gas mixture estimated in Kcal/h m °C using the following equation:

$$k_g = \Sigma k_i (M_i)^{0.33} p_i / M_i^{0.33} p_i$$

Density of the gas mixture estimated in Kg/m^3:

$$\rho_g = p M/R T$$

Average molecular weight of the reactant mixture in kg/kgmol:

$$M = \Sigma p_i M_i / P$$

Viscosity of the reactant mixture estimated in Kg/m h:

$$\mu_g = \Sigma u_i M_i^{0.5} p_i / M_i^{0.5} p_i$$

Heat capacity of the coolant in Kcal/kg °C:

$$Cp_c = 0.00035 * Tc + 0.348$$

Thermal conductivity of the coolant in Kcal/h m °C:

$$kc = -0.00005 * Tc + 0.1267$$

Viscosity of the coolant in Kg/m h:

$$\mu c = -0.0026 * Tc + 3.137$$

NOMENCLATURE

a	kinetic parameter (E/R2)	[-]
b	pre-exponential kinetic factor	[-]
C_p	heat capacity	[KJ/kg/K]
D_{er}	effective radial diffusivity	[m2/h]
d_p	particle diameter or equivalent diameter	[m]
E	energy of activation	[KJ/kmol]
h_{out}	coolant jacket side heat transfer coefficient	[KJ/h/m2/K]
k_{er}	effective radial thermal conductivity	[KJ/h/m2/K]
k_g	thermal conductivity of gas	[KJ/h/m2/K]
M	molecular weight	[kg/kmol]
p	pressure	[kPa]
R	reactor radius	[m]
T	temperature	[K]
T_c	coolant temperature	[K]
U	overall heat transfer coefficient	[KJ/h/m2/K]
u_s	superficial velocity	[m/s]
W_c	coolant flow rate	[kg/h]
z	axial coordinate	[m]
Pe	Peclet number	[-]
Pr	Prandtl number	[-]
Re	Reynolds number	[-]
α_w	heat transfer coefficient near the wall	[KJ/h/m2/K]
ρ	density	[kg/m3]
μ	viscosity	[kg/m/h]
ΔH	enthalpy of reaction	[KJ/kmol]

Appendix L

Simulation results (PO reactor).

```
              *****************************************
              *                                       *
              *               SIMULATION              *
              *                                       *
              *              RUN P0880201             *
              *                                       *
              *****************************************


*******************************
    SIMULATION CONDITIONS
*******************************

        Total pressure: 34.0 atm
  Reactant temperature: 358.2 C
         Reactant flow: 16.80 l/min
                H2/CO: 1.05
   Coolant temperature: 361.3 C
          Coolant flow:  8.2 kg/hr
         Test duration: 170 min
        Time on stream: 14.4 hr


*************************
  ESTIMATED PARAMETERS
*************************

       Enthalpy of reaction: -30817.0 Kcal/Kmol
      Preexponential factor:  9.77
  Heat transfer coefficient:  91.2 Kcal/m**2*h*K


****************
    RESULTS
****************

   Final product temperature: 380.61 C
          Final product flow: 15.53 l/min
   Final coolant temperature: 374.27 C

               CO conversion: 16.0 %
               H2 conversion:  8.9 %

        Product distribution:     CO2   71.5
                                  H2O    2.3
                                  HC    24.2
                                  CH3OH  2.0
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	362.41	361.26	1.15
.080	364.59	361.38	3.21
.120	365.79	361.58	4.22
.160	366.53	361.81	4.72
.200	367.04	362.06	4.98
.240	367.44	362.32	5.12
.280	367.79	362.58	5.20
.320	368.11	362.85	5.26
.360	368.42	363.12	5.29
.400	368.72	363.40	5.33
.440	369.03	363.67	5.35
.480	369.33	363.95	5.38
.520	369.63	364.22	5.41
.560	369.94	364.50	5.44
.600	370.24	364.78	5.46
.640	370.55	365.06	5.49
.680	370.86	365.35	5.51
.720	371.17	365.63	5.54
.760	371.48	365.91	5.57
.800	371.79	366.20	5.59
.840	372.11	366.49	5.62
.880	372.42	366.78	5.65
.920	372.74	367.07	5.67
.960	373.06	367.36	5.70
1.000	373.38	367.65	5.73
1.040	373.70	367.94	5.75
1.080	374.02	368.24	5.78
1.120	374.34	368.53	5.81
1.160	374.67	368.83	5.84
1.200	375.00	369.13	5.87
1.240	375.33	369.43	5.89
1.280	375.66	369.73	5.92
1.320	375.99	370.04	5.95
1.360	376.32	370.34	5.98
1.400	376.65	370.65	6.01
1.440	376.99	370.96	6.03
1.480	377.33	371.26	6.06
1.520	377.67	371.57	6.09
1.560	378.01	371.89	6.12
1.600	378.35	372.20	6.15
1.640	378.69	372.51	6.18
1.680	379.04	372.83	6.21
1.720	379.38	373.15	6.24
1.760	379.73	373.46	6.27
1.800	380.08	373.78	6.30
1.840	380.43	374.10	6.33

```
              ****************************************
              *                                      *
              *               SIMULATION             *
              *                                      *
              *              RUN P0880203            *
              *                                      *
              ****************************************

******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 372.2 C
         Reactant flow:  3.27 l/min
                H2/CO:  .96
   Coolant temperature: 372.2 C
          Coolant flow:  8.2 kg/hr
         Test duration: 195 min
        Time on stream: 20.5 hr

************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -19278.4 Kcal/Kmol
      Preexponential factor:  7.65
  Heat transfer coefficient: 103.8 Kcal/m**2*h*K

***************
    RESULTS
***************

   Final product temperature: 380.48 C
          Final product flow:  2.44 l/min
   Final coolant temperature: 378.71 C

               CO conversion: 49.8 %
               H2 conversion: 29.7 %

        Product distribution:     CO2    72.4
                                  H2O     2.8
                                  HC     24.4
                                  CH3OH    .5
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	375.90	372.36	3.54
.080	376.07	372.57	3.50
.120	376.18	372.77	3.41
.160	376.29	372.96	3.33
.200	376.41	373.15	3.26
.240	376.52	373.34	3.18
.280	376.64	373.52	3.12
.320	376.75	373.70	3.06
.360	376.87	373.87	3.00
.400	376.98	374.04	2.94
.440	377.10	374.21	2.89
.480	377.21	374.37	2.84
.520	377.32	374.53	2.79
.560	377.43	374.69	2.75
.600	377.55	374.84	2.70
.640	377.66	375.00	2.66
.680	377.77	375.15	2.62
.720	377.87	375.29	2.58
.760	377.98	375.44	2.54
.800	378.09	375.58	2.51
.840	378.19	375.72	2.47
.880	378.30	375.86	2.44
.920	378.40	376.00	2.41
.960	378.50	376.13	2.37
1.000	378.60	376.26	2.34
1.040	378.70	376.39	2.31
1.080	378.80	376.52	2.28
1.120	378.90	376.65	2.25
1.160	379.00	376.77	2.22
1.200	379.09	376.90	2.19
1.240	379.19	377.02	2.17
1.280	379.28	377.14	2.14
1.320	379.37	377.26	2.11
1.360	379.46	377.37	2.09
1.400	379.55	377.49	2.06
1.440	379.64	377.60	2.03
1.480	379.72	377.71	2.01
1.520	379.81	377.83	1.98
1.560	379.89	377.93	1.96
1.600	379.97	378.04	1.93
1.640	380.05	378.15	1.91
1.680	380.13	378.25	1.88
1.720	380.21	378.36	1.86
1.760	380.29	378.46	1.83
1.800	380.37	378.56	1.81
1.840	380.44	378.66	1.78

```
              **************************************
              *                                    *
              *             SIMULATION             *
              *                                    *
              *           RUN P0880204             *
              *                                    *
              **************************************

*****************************
   SIMULATION CONDITIONS
*****************************

        Total pressure: 34.0 atm
  Reactant temperature: 353.7 C
         Reactant flow:  3.24 l/min
                H2/CO:  .96
   Coolant temperature: 353.7 C
          Coolant flow:  8.2 kg/hr
         Test duration: 225 min
        Time on stream: 26.0 hr

***********************
  ESTIMATED PARAMETERS
***********************

       Enthalpy of reaction: -28259.0 Kcal/Kmol
     Preexponential factor: 10.22
  Heat transfer coefficient: 231.3 Kcal/m**2*h*K

**************
   RESULTS
**************

   Final product temperature: 361.25 C
          Final product flow:  2.60 l/min
   Final coolant temperature: 360.33 C

              CO conversion: 39.5 %
              H2 conversion: 23.0 %

       Product distribution:      CO2    72.5
                                  H2O     2.0
                                  HC     24.8
                                  CH3OH    .7
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	355.22	353.86	1.36
.080	355.38	354.04	1.34
.120	355.54	354.21	1.33
.160	355.70	354.39	1.31
.200	355.86	354.56	1.30
.240	356.01	354.73	1.29
.280	356.16	354.89	1.27
.320	356.32	355.06	1.26
.360	356.47	355.22	1.25
.400	356.62	355.38	1.24
.440	356.76	355.54	1.22
.480	356.91	355.70	1.21
.520	357.05	355.85	1.20
.560	357.20	356.01	1.19
.600	357.34	356.16	1.18
.640	357.48	356.31	1.17
.680	357.62	356.46	1.16
.720	357.76	356.61	1.15
.760	357.90	356.76	1.14
.800	358.03	356.90	1.13
.840	358.17	357.05	1.12
.880	358.30	357.19	1.11
.920	358.43	357.33	1.10
.960	358.56	357.47	1.09
1.000	358.69	357.61	1.08
1.040	358.82	357.75	1.07
1.080	358.95	357.89	1.07
1.120	359.08	358.02	1.06
1.160	359.20	358.16	1.05
1.200	359.33	358.29	1.04
1.240	359.45	358.42	1.03
1.280	359.58	358.55	1.02
1.320	359.70	358.68	1.02
1.360	359.82	358.81	1.01
1.400	359.94	358.94	1.00
1.440	360.06	359.07	.99
1.480	360.18	359.19	.99
1.520	360.29	359.32	.98
1.560	360.41	359.44	.97
1.600	360.52	359.56	.96
1.640	360.64	359.68	.95
1.680	360.75	359.80	.95
1.720	360.86	359.92	.94
1.760	360.97	360.04	.93
1.800	361.08	360.16	.93
1.840	361.19	360.28	.92

```
                          ***************************************
                          *                                     *
                          *              SIMULATION             *
                          *                                     *
                          *            RUN P0880208             *
                          *                                     *
                          ***************************************

*****************************
   SIMULATION CONDITIONS
*****************************

        Total pressure: 34.0 atm
  Reactant temperature: 368.7 C
         Reactant flow:  5.84 l/min
                H2/CO: 1.06
   Coolant temperature: 368.7 C
          Coolant flow:  8.2 kg/hr
         Test duration: 185 min
        Time on stream: 31.4 hr


***********************
  ESTIMATED PARAMETERS
***********************

      Enthalpy of reaction: -31257.2 Kcal/Kmol
     Preexponential factor:  6.21
  Heat transfer coefficient: 123.9 Kcal/m**2*h*K


**************
   RESULTS
**************

   Final product temperature: 380.09 C
          Final product flow:  5.04 l/min
   Final coolant temperature: 377.54 C

              CO conversion: 29.0 %
              H2 conversion: 15.6 %

        Product distribution:      CO2    69.8
                                   H2O     2.5
                                   HC     27.0
                                   CH3OH    .7
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	371.77	368.85	2.92
.080	372.12	369.06	3.06
.120	372.32	369.27	3.05
.160	372.52	369.48	3.04
.200	372.71	369.69	3.02
.240	372.90	369.90	3.00
.280	373.10	370.11	2.99
.320	373.29	370.31	2.97
.360	373.48	370.52	2.96
.400	373.67	370.72	2.94
.440	373.86	370.93	2.93
.480	374.04	371.13	2.91
.520	374.23	371.33	2.90
.560	374.42	371.53	2.89
.600	374.60	371.73	2.87
.640	374.79	371.93	2.86
.680	374.97	372.12	2.85
.720	375.15	372.32	2.84
.760	375.34	372.51	2.82
.800	375.52	372.71	2.81
.840	375.70	372.90	2.80
.880	375.88	373.09	2.79
.920	376.06	373.28	2.78
.960	376.24	373.47	2.77
1.000	376.42	373.66	2.75
1.040	376.59	373.85	2.74
1.080	376.77	374.04	2.73
1.120	376.95	374.22	2.72
1.160	377.12	374.41	2.71
1.200	377.30	374.59	2.70
1.240	377.47	374.78	2.69
1.280	377.64	374.96	2.68
1.320	377.82	375.14	2.67
1.360	377.99	375.33	2.66
1.400	378.16	375.51	2.65
1.440	378.33	375.69	2.64
1.480	378.50	375.87	2.63
1.520	378.67	376.05	2.63
1.560	378.84	376.22	2.62
1.600	379.01	376.40	2.61
1.640	379.18	376.58	2.60
1.680	379.35	376.76	2.59
1.720	379.51	376.93	2.58
1.760	379.68	377.11	2.57
1.800	379.84	377.28	2.56
1.840	380.01	377.45	2.56

```
              ****************************************
              *                                      *
              *              SIMULATION              *
              *                                      *
              *             RUN P0880210             *
              *                                      *
              ****************************************

******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 20.0 atm
  Reactant temperature: 370.9 C
         Reactant flow:  2.35 l/min
                H2/CO:   .96
   Coolant temperature: 370.9 C
          Coolant flow:  8.2 kg/hr
         Test duration: 185 min
        Time on stream: 36.5 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -26344.8 Kcal/Kmol
      Preexponential factor:  7.58
  Heat transfer coefficient: 263.7 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 375.44 C
          Final product flow:  1.94 l/min
   Final coolant temperature: 374.98 C

               CO conversion: 35.5 %
               H2 conversion: 20.8 %

        Product distribution:      CO2    72.4
                                   H2O     2.3
                                   HC     24.8
                                   CH3OH    .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	371.78	371.01	.78
.080	371.89	371.12	.76
.120	371.99	371.23	.75
.160	372.09	371.35	.74
.200	372.19	371.45	.73
.240	372.28	371.56	.72
.280	372.38	371.67	.71
.320	372.47	371.77	.70
.360	372.57	371.87	.69
.400	372.66	371.98	.69
.440	372.75	372.08	.68
.480	372.84	372.18	.67
.520	372.93	372.27	.66
.560	373.02	372.37	.65
.600	373.11	372.47	.64
.640	373.20	372.56	.64
.680	373.28	372.65	.63
.720	373.37	372.74	.62
.760	373.45	372.84	.61
.800	373.53	372.93	.61
.840	373.61	373.01	.60
.880	373.70	373.10	.59
.920	373.78	373.19	.59
.960	373.85	373.27	.58
1.000	373.93	373.36	.57
1.040	374.01	373.44	.57
1.080	374.09	373.53	.56
1.120	374.16	373.61	.56
1.160	374.24	373.69	.55
1.200	374.31	373.77	.54
1.240	374.39	373.85	.54
1.280	374.46	373.93	.53
1.320	374.53	374.01	.53
1.360	374.60	374.08	.52
1.400	374.67	374.16	.52
1.440	374.74	374.23	.51
1.480	374.81	374.31	.51
1.520	374.88	374.38	.50
1.560	374.95	374.46	.50
1.600	375.02	374.53	.49
1.640	375.08	374.60	.49
1.680	375.15	374.67	.48
1.720	375.22	374.74	.48
1.760	375.28	374.81	.47
1.800	375.34	374.88	.47
1.840	375.41	374.95	.46

```
                    ***************************************
                    *                                     *
                    *              SIMULATION             *
                    *                                     *
                    *            RUN P0880212             *
                    *                                     *
                    ***************************************

*****************************
    SIMULATION CONDITIONS
*****************************

        Total pressure: 34.0 atm
  Reactant temperature: 371.3 C
         Reactant flow:  3.27 l/min
                H2/CO:  .96
   Coolant temperature: 371.3 C
          Coolant flow:  8.2 kg/hr
         Test duration: 260 min
        Time on stream: 42.2 hr

***********************
  ESTIMATED PARAMETERS
***********************

       Enthalpy of reaction: -36239.2 Kcal/Kmol
      Preexponential factor:  2.87
  Heat transfer coefficient:  75.8 Kcal/m**2*h*K

**************
   RESULTS
**************

   Final product temperature: 378.15 C
          Final product flow:  2.90 l/min
   Final coolant temperature: 376.02 C

              CO conversion: 23.4 %
              H2 conversion: 13.6 %

       Product distribution:     CO2    70.9
                                 H2O     2.1
                                 HC     26.6
                                 CH3OH    .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	374.08	371.38	2.70
.080	374.29	371.50	2.79
.120	374.39	371.62	2.77
.160	374.49	371.74	2.75
.200	374.58	371.85	2.73
.240	374.67	371.97	2.71
.280	374.77	372.08	2.69
.320	374.86	372.20	2.67
.360	374.96	372.31	2.65
.400	375.05	372.42	2.63
.440	375.14	372.53	2.61
.480	375.23	372.64	2.59
.520	375.32	372.75	2.57
.560	375.41	372.86	2.56
.600	375.50	372.97	2.54
.640	375.59	373.07	2.52
.680	375.68	373.18	2.50
.720	375.77	373.28	2.49
.760	375.86	373.39	2.47
.800	375.95	373.49	2.46
.840	376.04	373.60	2.44
.880	376.13	373.70	2.43
.920	376.21	373.80	2.41
.960	376.30	373.90	2.40
1.000	376.39	374.00	2.38
1.040	376.47	374.10	2.37
1.080	376.56	374.20	2.36
1.120	376.64	374.30	2.34
1.160	376.73	374.40	2.33
1.200	376.81	374.49	2.32
1.240	376.89	374.59	2.30
1.280	376.98	374.69	2.29
1.320	377.06	374.78	2.28
1.360	377.14	374.88	2.27
1.400	377.23	374.97	2.25
1.440	377.31	375.07	2.24
1.480	377.39	375.16	2.23
1.520	377.47	375.25	2.22
1.560	377.55	375.35	2.21
1.600	377.63	375.44	2.20
1.640	377.71	375.53	2.19
1.680	377.79	375.62	2.17
1.720	377.87	375.71	2.16
1.760	377.95	375.80	2.15
1.800	378.03	375.89	2.14
1.840	378.11	375.98	2.13

```
              ****************************************
              *                                      *
              *              SIMULATION              *
              *                                      *
              *             RUN P0880225             *
              *                                      *
              ****************************************


******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 376.3 C
         Reactant flow: 16.70 l/min
                 H2/CO: 1.04
   Coolant temperature: 376.4 C
          Coolant flow:  8.2 kg/hr
         Test duration: 200 min
        Time on stream: 48.0 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -30345.8 Kcal/Kmol
      Preexponential factor:  6.51
  Heat transfer coefficient: 103.0 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 395.81 C
          Final product flow: 15.39 l/min
   Final coolant temperature: 390.16 C

              CO conversion: 17.1 %
              H2 conversion:  9.6 %

        Product distribution:     CO2    66.5
                                  H2O     2.5
                                  HC     29.8
                                  CH3OH   1.3
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	379.29	376.49	2.80
.080	380.74	376.69	4.05
.120	381.54	376.94	4.59
.160	382.05	377.22	4.84
.200	382.45	377.50	4.95
.240	382.79	377.78	5.01
.280	383.12	378.07	5.04
.320	383.43	378.36	5.07
.360	383.74	378.66	5.08
.400	384.05	378.95	5.10
.440	384.36	379.24	5.12
.480	384.67	379.54	5.13
.520	384.98	379.83	5.15
.560	385.29	380.13	5.16
.600	385.60	380.42	5.18
.640	385.91	380.72	5.19
.680	386.23	381.02	5.21
.720	386.54	381.32	5.22
.760	386.85	381.62	5.24
.800	387.17	381.92	5.25
.840	387.48	382.22	5.27
.880	387.80	382.52	5.28
.920	388.12	382.82	5.30
.960	388.44	383.13	5.31
1.000	388.76	383.43	5.33
1.040	389.08	383.74	5.34
1.080	389.40	384.04	5.35
1.120	389.72	384.35	5.37
1.160	390.04	384.66	5.38
1.200	390.36	384.96	5.40
1.240	390.69	385.27	5.42
1.280	391.01	385.58	5.43
1.320	391.34	385.89	5.45
1.360	391.67	386.21	5.46
1.400	391.99	386.52	5.48
1.440	392.32	386.83	5.49
1.480	392.65	387.14	5.51
1.520	392.98	387.46	5.52
1.560	393.31	387.77	5.54
1.600	393.64	388.09	5.55
1.640	393.97	388.41	5.57
1.680	394.31	388.72	5.58
1.720	394.64	389.04	5.60
1.760	394.97	389.36	5.61
1.800	395.31	389.68	5.63
1.840	395.64	390.00	5.64

```
              ****************************************
              *                                      *
              *              SIMULATION              *
              *                                      *
              *             RUN P0880302             *
              *                                      *
              ****************************************


******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 375.5 C
         Reactant flow: 16.10 l/min
                 H2/CO: 1.04
   Coolant temperature: 376.6 C
          Coolant flow:  8.2 kg/hr
         Test duration: 195 min
        Time on stream: 53.3 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -36898.8 Kcal/Kmol
      Preexponential factor:  6.06
  Heat transfer coefficient: 113.7 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 398.40 C
          Final product flow: 14.79 l/min
   Final coolant temperature: 392.34 C

               CO conversion: 17.2 %
               H2 conversion:  9.7 %

        Product distribution:     CO2    71.5
                                  H2O     2.8
                                  HC     24.4
                                  CH3OH   1.3
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	379.32	376.67	2.65
.080	380.99	376.89	4.10
.120	381.85	377.17	4.68
.160	382.39	377.48	4.91
.200	382.81	377.79	5.02
.240	383.19	378.11	5.08
.280	383.55	378.44	5.11
.320	383.90	378.76	5.14
.360	384.25	379.09	5.16
.400	384.60	379.42	5.19
.440	384.96	379.75	5.21
.480	385.31	380.08	5.23
.520	385.67	380.41	5.25
.560	386.02	380.74	5.28
.600	386.38	381.08	5.30
.640	386.74	381.42	5.32
.680	387.10	381.75	5.35
.720	387.46	382.09	5.37
.760	387.82	382.43	5.39
.800	388.19	382.77	5.42
.840	388.56	383.12	5.44
.880	388.92	383.46	5.46
.920	389.29	383.81	5.49
.960	389.66	384.15	5.51
1.000	390.04	384.50	5.53
1.040	390.41	384.85	5.56
1.080	390.79	385.20	5.58
1.120	391.16	385.56	5.60
1.160	391.54	385.91	5.63
1.200	391.92	386.27	5.65
1.240	392.30	386.62	5.68
1.280	392.68	386.98	5.70
1.320	393.07	387.34	5.73
1.360	393.45	387.70	5.75
1.400	393.84	388.07	5.78
1.440	394.23	388.43	5.80
1.480	394.62	388.79	5.82
1.520	395.01	389.16	5.85
1.560	395.40	389.53	5.87
1.600	395.80	389.90	5.90
1.640	396.19	390.27	5.92
1.680	396.59	390.64	5.95
1.720	396.99	391.02	5.97
1.760	397.39	391.39	6.00
1.800	397.79	391.77	6.03
1.840	398.20	392.15	6.05

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                    ****************************************
                    *                                      *
                    *              SIMULATION              *
                    *                                      *
                    *            RUN P0880304              *
                    *                                      *
                    ****************************************

    ******************************
       SIMULATION CONDITIONS
    ******************************

              Total pressure: 34.0 atm
        Reactant temperature: 365.4 C
               Reactant flow: 16.90 l/min
                       H2/CO: 1.41
         Coolant temperature: 366.0 C
                Coolant flow:  8.2 kg/hr
               Test duration: 200 min
              Time on stream: 58.6 hr

    ************************
      ESTIMATED PARAMETERS
    ************************

             Enthalpy of reaction: -36626.8 Kcal/Kmol
           Preexponential factor:  6.93
       Heat transfer coefficient: 104.0 Kcal/m**2*h*K

    ***************
       RESULTS
    ***************

       Final product temperature: 384.16 C
              Final product flow: 15.83 l/min
       Final coolant temperature: 378.72 C

                   CO conversion: 15.6 %
                   H2 conversion:  6.7 %

            Product distribution:      CO2    69.7
                                       H2O     3.2
                                       HC     25.3
                                       CH3OH   1.8
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	368.26	366.06	2.21
.080	369.64	366.23	3.41
.120	370.39	366.45	3.95
.160	370.87	366.68	4.19
.200	371.23	366.93	4.30
.240	371.55	367.19	4.36
.280	371.85	367.44	4.40
.320	372.13	367.70	4.43
.360	372.42	367.96	4.46
.400	372.71	368.22	4.48
.440	372.99	368.48	4.51
.480	373.28	368.75	4.53
.520	373.57	369.01	4.55
.560	373.86	369.28	4.58
.600	374.15	369.55	4.60
.640	374.44	369.82	4.63
.680	374.74	370.09	4.65
.720	375.03	370.36	4.67
.760	375.33	370.63	4.70
.800	375.63	370.91	4.72
.840	375.93	371.18	4.75
.880	376.23	371.46	4.77
.920	376.54	371.74	4.80
.960	376.84	372.02	4.82
1.000	377.15	372.30	4.85
1.040	377.46	372.58	4.88
1.080	377.77	372.87	4.90
1.120	378.08	373.15	4.93
1.160	378.40	373.44	4.95
1.200	378.71	373.73	4.98
1.240	379.03	374.02	5.01
1.280	379.35	374.31	5.03
1.320	379.67	374.61	5.06
1.360	379.99	374.90	5.09
1.400	380.31	375.20	5.12
1.440	380.64	375.49	5.14
1.480	380.97	375.79	5.17
1.520	381.29	376.09	5.20
1.560	381.63	376.40	5.23
1.600	381.96	376.70	5.26
1.640	382.29	377.01	5.29
1.680	382.63	377.31	5.32
1.720	382.97	377.62	5.34
1.760	383.31	377.93	5.37
1.800	383.65	378.24	5.40
1.840	383.99	378.56	5.43

```
              ***************************************
              *                                     *
              *             SIMULATION              *
              *                                     *
              *            RUN P0880307             *
              *                                     *
              ***************************************


******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 365.9 C
         Reactant flow: 15.70 l/min
                H2/CO:  .73
   Coolant temperature: 367.6 C
          Coolant flow:  8.2 kg/hr
         Test duration: 175 min
        Time on stream: 63.7 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -29820.0 Kcal/Kmol
      Preexponential factor:  8.35
  Heat transfer coefficient: 106.2 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 383.10 C
          Final product flow: 14.59 l/min
   Final coolant temperature: 378.77 C

               CO conversion: 12.8 %
               H2 conversion:  9.8 %

        Product distribution:     CO2    71.5
                                  H2O     1.6
                                  HC     25.4
                                  CH3OH   1.5
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	369.39	367.62	1.77
.080	370.91	367.77	3.14
.120	371.65	367.98	3.68
.160	372.10	368.20	3.89
.200	372.42	368.44	3.98
.240	372.70	368.68	4.02
.280	372.96	368.92	4.04
.320	373.22	369.16	4.06
.360	373.47	369.40	4.07
.400	373.72	369.65	4.08
.440	373.97	369.89	4.09
.480	374.23	370.13	4.09
.520	374.48	370.38	4.10
.560	374.73	370.62	4.11
.600	374.98	370.87	4.12
.640	375.24	371.11	4.13
.680	375.49	371.36	4.13
.720	375.74	371.60	4.14
.760	376.00	371.85	4.15
.800	376.25	372.10	4.16
.840	376.51	372.34	4.16
.880	376.76	372.59	4.17
.920	377.02	372.84	4.18
.960	377.27	373.09	4.19
1.000	377.53	373.34	4.19
1.040	377.79	373.59	4.20
1.080	378.04	373.84	4.21
1.120	378.30	374.09	4.22
1.160	378.56	374.34	4.22
1.200	378.82	374.59	4.23
1.240	379.07	374.84	4.24
1.280	379.33	375.09	4.24
1.320	379.59	375.34	4.25
1.360	379.85	375.59	4.26
1.400	380.11	375.85	4.26
1.440	380.37	376.10	4.27
1.480	380.63	376.35	4.28
1.520	380.89	376.60	4.28
1.560	381.15	376.86	4.29
1.600	381.41	377.11	4.29
1.640	381.67	377.37	4.30
1.680	381.93	377.62	4.31
1.720	382.19	377.88	4.31
1.760	382.45	378.13	4.32
1.800	382.71	378.39	4.32
1.840	382.97	378.64	4.33

```
              ****************************************
              *                                      *
              *             SIMULATION               *
              *                                      *
              *            RUN P0880308              *
              *                                      *
              ****************************************


*****************************
    SIMULATION CONDITIONS
*****************************

        Total pressure: 34.0 atm
  Reactant temperature: 369.8 C
         Reactant flow:  3.19 l/min
                H2/CO:  .96
   Coolant temperature: 369.8 C
          Coolant flow:  8.2 kg/hr
         Test duration: 190 min
        Time on stream: 68.7 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -47386.2 Kcal/Kmol
      Preexponential factor:  2.33
  Heat transfer coefficient:  42.2 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 378.96 C
          Final product flow:  2.87 l/min
   Final coolant temperature: 374.83 C

               CO conversion: 20.6 %
               H2 conversion: 12.0 %

        Product distribution:    CO2   70.7
                                 H2O    2.1
                                 HC    26.8
                                 CH3OH   .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	374.15	369.86	4.28
.080	375.06	369.98	5.08
.120	375.31	370.10	5.21
.160	375.43	370.22	5.20
.200	375.52	370.35	5.17
.240	375.61	370.47	5.14
.280	375.69	370.59	5.10
.320	375.78	370.71	5.07
.360	375.87	370.83	5.04
.400	375.95	370.95	5.00
.440	376.04	371.07	4.97
.480	376.12	371.18	4.94
.520	376.21	371.30	4.91
.560	376.30	371.41	4.88
.600	376.38	371.53	4.85
.640	376.47	371.64	4.82
.680	376.55	371.76	4.79
.720	376.64	371.87	4.77
.760	376.72	371.98	4.74
.800	376.80	372.09	4.71
.840	376.89	372.20	4.69
.880	376.97	372.31	4.66
.920	377.06	372.42	4.63
.960	377.14	372.53	4.61
1.000	377.22	372.64	4.58
1.040	377.31	372.75	4.56
1.080	377.39	372.85	4.54
1.120	377.47	372.96	4.51
1.160	377.56	373.07	4.49
1.200	377.64	373.17	4.47
1.240	377.72	373.28	4.44
1.280	377.80	373.38	4.42
1.320	377.88	373.48	4.40
1.360	377.96	373.59	4.38
1.400	378.05	373.69	4.36
1.440	378.13	373.79	4.34
1.480	378.21	373.89	4.32
1.520	378.29	373.99	4.30
1.560	378.37	374.09	4.28
1.600	378.45	374.19	4.26
1.640	378.53	374.29	4.24
1.680	378.61	374.39	4.22
1.720	378.69	374.49	4.20
1.760	378.77	374.59	4.18
1.800	378.85	374.68	4.16
1.840	378.92	374.78	4.14

```
              **************************************
              *                                    *
              *            SIMULATION              *
              *                                    *
              *           RUN P0880309             *
              *                                    *
              **************************************

*****************************
   SIMULATION CONDITIONS
*****************************

         Total pressure: 34.0 atm
  Reactant temperature: 349.9 C
          Reactant flow: 16.80 l/min
                  H2/CO: 1.05
   Coolant temperature: 351.2 C
           Coolant flow:  8.2 kg/hr
          Test duration: 170 min
         Time on stream: 73.7 hr

***********************
  ESTIMATED PARAMETERS
***********************

      Enthalpy of reaction: -21362.2 Kcal/Kmol
     Preexponential factor: 11.00
  Heat transfer coefficient:  89.4 Kcal/m**2*h*K

***************
   RESULTS
***************

   Final product temperature: 361.02 C
          Final product flow: 15.93 l/min
   Final coolant temperature: 357.91 C

              CO conversion: 10.9 %
              H2 conversion:  6.0 %

        Product distribution:      CO2    69.6
                                   H2O     1.8
                                   HC     26.0
                                   CH3OH   2.6
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	352.12	351.20	.92
.080	353.23	351.27	1.95
.120	353.82	351.39	2.43
.160	354.17	351.52	2.66
.200	354.42	351.65	2.76
.240	354.61	351.80	2.82
.280	354.78	351.94	2.84
.320	354.94	352.08	2.86
.360	355.10	352.23	2.87
.400	355.25	352.38	2.88
.440	355.41	352.52	2.88
.480	355.56	352.67	2.89
.520	355.71	352.82	2.90
.560	355.87	352.96	2.90
.600	356.02	353.11	2.91
.640	356.17	353.26	2.92
.680	356.33	353.41	2.92
.720	356.48	353.55	2.93
.760	356.64	353.70	2.94
.800	356.79	353.85	2.94
.840	356.95	354.00	2.95
.880	357.10	354.15	2.95
.920	357.26	354.30	2.96
.960	357.42	354.45	2.97
1.000	357.57	354.60	2.97
1.040	357.73	354.75	2.98
1.080	357.89	354.90	2.99
1.120	358.05	355.05	2.99
1.160	358.20	355.20	3.00
1.200	358.36	355.36	3.01
1.240	358.52	355.51	3.01
1.280	358.68	355.66	3.02
1.320	358.84	355.81	3.03
1.360	359.00	355.97	3.03
1.400	359.16	356.12	3.04
1.440	359.32	356.27	3.04
1.480	359.48	356.43	3.05
1.520	359.64	356.58	3.06
1.560	359.80	356.74	3.06
1.600	359.96	356.89	3.07
1.640	360.13	357.05	3.08
1.680	360.29	357.20	3.08
1.720	360.45	357.36	3.09
1.760	360.61	357.52	3.10
1.800	360.78	357.67	3.10
1.840	360.94	357.83	3.11

```
              ****************************************
              *                                      *
              *              SIMULATION              *
              *                                      *
              *             RUN P0880314             *
              *                                      *
              ****************************************


******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 368.5 C
         Reactant flow: 16.70 l/min
                 H2/CO:  .99
   Coolant temperature: 369.8 C
          Coolant flow: 16.6 kg/hr
         Test duration: 155 min
        Time on stream: 78.4 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -32456.4 Kcal/Kmol
      Preexponential factor: 10.75
  Heat transfer coefficient: 383.3 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 379.64 C
          Final product flow: 15.23 l/min
   Final coolant temperature: 377.99 C

               CO conversion: 18.1 %
               H2 conversion: 10.6 %

        Product distribution:     CO2    71.8
                                  H2O     2.2
                                  HC     24.2
                                  CH3OH   1.8
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	371.53	369.89	1.64
.080	371.81	370.07	1.74
.120	371.99	370.26	1.74
.160	372.17	370.44	1.73
.200	372.35	370.63	1.73
.240	372.54	370.81	1.73
.280	372.72	370.99	1.72
.320	372.90	371.18	1.72
.360	373.08	371.36	1.72
.400	373.26	371.54	1.72
.440	373.44	371.72	1.72
.480	373.62	371.90	1.71
.520	373.80	372.08	1.71
.560	373.97	372.26	1.71
.600	374.15	372.45	1.71
.640	374.33	372.63	1.71
.680	374.51	372.81	1.70
.720	374.69	372.98	1.70
.760	374.86	373.16	1.70
.800	375.04	373.34	1.70
.840	375.22	373.52	1.70
.880	375.39	373.70	1.69
.920	375.57	373.88	1.69
.960	375.75	374.06	1.69
1.000	375.92	374.24	1.69
1.040	376.10	374.41	1.69
1.080	376.27	374.59	1.68
1.120	376.45	374.77	1.68
1.160	376.62	374.94	1.68
1.200	376.80	375.12	1.68
1.240	376.97	375.30	1.68
1.280	377.15	375.47	1.68
1.320	377.32	375.65	1.67
1.360	377.49	375.82	1.67
1.400	377.67	376.00	1.67
1.440	377.84	376.17	1.67
1.480	378.01	376.35	1.67
1.520	378.19	376.52	1.67
1.560	378.36	376.70	1.66
1.600	378.53	376.87	1.66
1.640	378.70	377.04	1.66
1.680	378.87	377.22	1.66
1.720	379.05	377.39	1.66
1.760	379.22	377.56	1.66
1.800	379.39	377.73	1.65
1.840	379.56	377.91	1.65

```
                  ***************************************
                  *                                     *
                  *             SIMULATION              *
                  *                                     *
                  *           RUN P0880316              *
                  *                                     *
                  ***************************************

******************************
    SIMULATION CONDITIONS
******************************

         Total pressure: 34.0 atm
  Reactant temperature: 381.8 C
          Reactant flow:  3.36 l/min
                  H2/CO:  .79
   Coolant temperature: 381.8 C
           Coolant flow:  8.2 kg/hr
          Test duration: 185 min
         Time on stream: 83.3 hr

************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -29669.2 Kcal/Kmol
      Preexponential factor:  4.69
  Heat transfer coefficient: 126.4 Kcal/m**2*h*K

***************
    RESULTS
***************

   Final product temperature: 390.61 C
          Final product flow:  2.70 l/min
   Final coolant temperature: 388.97 C

              CO conversion: 36.7 %
              H2 conversion: 25.9 %

         Product distribution:      CO2    72.5
                                    H2O     2.1
                                    HC     25.0
                                    CH3OH    .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	385.11	381.98	3.13
.080	385.28	382.20	3.08
.120	385.43	382.41	3.01
.160	385.57	382.62	2.95
.200	385.72	382.83	2.90
.240	385.87	383.03	2.84
.280	386.01	383.22	2.79
.320	386.16	383.42	2.74
.360	386.30	383.60	2.69
.400	386.44	383.79	2.65
.440	386.58	383.97	2.61
.480	386.72	384.15	2.56
.520	386.85	384.33	2.52
.560	386.99	384.50	2.49
.600	387.12	384.67	2.45
.640	387.25	384.84	2.41
.680	387.38	385.00	2.38
.720	387.51	385.17	2.35
.760	387.64	385.33	2.31
.800	387.77	385.48	2.28
.840	387.89	385.64	2.25
.880	388.02	385.79	2.22
.920	388.14	385.94	2.19
.960	388.26	386.09	2.16
1.000	388.38	386.24	2.14
1.040	388.50	386.39	2.11
1.080	388.61	386.53	2.08
1.120	388.73	386.67	2.06
1.160	388.84	386.81	2.03
1.200	388.95	386.95	2.01
1.240	389.06	387.08	1.98
1.280	389.17	387.21	1.96
1.320	389.28	387.35	1.93
1.360	389.39	387.48	1.91
1.400	389.49	387.61	1.89
1.440	389.60	387.73	1.86
1.480	389.70	387.86	1.84
1.520	389.80	387.98	1.82
1.560	389.90	388.10	1.80
1.600	390.00	388.22	1.77
1.640	390.10	388.34	1.75
1.680	390.19	388.46	1.73
1.720	390.29	388.58	1.71
1.760	390.38	388.69	1.69
1.800	390.47	388.80	1.67
1.840	390.56	388.92	1.65

```
               ****************************************
               *                                      *
               *              SIMULATION              *
               *                                      *
               *             RUN P0880317             *
               *                                      *
               ****************************************


******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 34.0 atm
  Reactant temperature: 381.4 C
         Reactant flow:  6.02 l/min
                 H2/CO:  .89
   Coolant temperature: 381.4 C
          Coolant flow:  8.2 kg/hr
         Test duration: 160 min
        Time on stream: 88.1 hr


************************
  ESTIMATED PARAMETERS
************************

       Enthalpy of reaction: -35209.6 Kcal/Kmol
      Preexponential factor:  5.09
  Heat transfer coefficient: 132.8 Kcal/m**2*h*K


***************
    RESULTS
***************

   Final product temperature: 395.34 C
          Final product flow:  5.15 l/min
   Final coolant temperature: 392.49 C

               CO conversion: 29.9 %
               H2 conversion: 19.0 %

        Product distribution:     CO2   69.1
                                  H2O    2.4
                                  HC    28.0
                                  CH3OH   .5
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	385.27	381.60	3.68
.080	385.70	381.88	3.83
.120	385.96	382.16	3.80
.160	386.21	382.44	3.77
.200	386.45	382.72	3.74
.240	386.69	382.99	3.71
.280	386.94	383.26	3.67
.320	387.18	383.53	3.64
.360	387.41	383.80	3.62
.400	387.65	384.06	3.59
.440	387.88	384.32	3.56
.480	388.12	384.58	3.53
.520	388.35	384.84	3.51
.560	388.58	385.10	3.48
.600	388.81	385.35	3.46
.640	389.04	385.60	3.43
.680	389.26	385.85	3.41
.720	389.49	386.10	3.39
.760	389.71	386.35	3.36
.800	389.93	386.59	3.34
.840	390.15	386.83	3.32
.880	390.37	387.07	3.30
.920	390.59	387.31	3.28
.960	390.81	387.55	3.25
1.000	391.02	387.79	3.23
1.040	391.23	388.02	3.21
1.080	391.45	388.25	3.19
1.120	391.66	388.48	3.18
1.160	391.87	388.71	3.16
1.200	392.08	388.94	3.14
1.240	392.29	389.17	3.12
1.280	392.49	389.39	3.10
1.320	392.70	389.61	3.08
1.360	392.90	389.84	3.06
1.400	393.10	390.06	3.05
1.440	393.30	390.28	3.03
1.480	393.50	390.49	3.01
1.520	393.70	390.71	2.99
1.560	393.90	390.92	2.98
1.600	394.10	391.14	2.96
1.640	394.29	391.35	2.94
1.680	394.48	391.56	2.92
1.720	394.68	391.77	2.91
1.760	394.87	391.98	2.89
1.800	395.06	392.18	2.87
1.840	395.25	392.39	2.86

```
              ****************************************
              *                                      *
              *              SIMULATION              *
              *                                      *
              *             RUN P0880318             *
              *                                      *
              ****************************************

******************************
    SIMULATION CONDITIONS
******************************

        Total pressure: 20.0 atm
  Reactant temperature: 366.9 C
         Reactant flow: 10.90 l/min
                H2/CO:  .95
   Coolant temperature: 369.3 C
          Coolant flow:  8.2 kg/hr
         Test duration: 165 min
        Time on stream: 92.8 hr

*************************
  ESTIMATED PARAMETERS
*************************

       Enthalpy of reaction: -20041.2 Kcal/Kmol
      Preexponential factor: 11.00
  Heat transfer coefficient: 100.6 Kcal/m**2*h*K

***************
    RESULTS
***************

   Final product temperature: 377.05 C
          Final product flow: 10.18 l/min
   Final coolant temperature: 374.92 C

               CO conversion: 13.9 %
               H2 conversion:  8.3 %

        Product distribution:     CO2    67.2
                                  H2O     1.9
                                  HC     29.5
                                  CH3OH   1.5
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	370.39	369.28	1.10
.080	371.38	369.38	2.01
.120	371.73	369.50	2.23
.160	371.91	369.63	2.28
.200	372.05	369.76	2.29
.240	372.17	369.89	2.29
.280	372.30	370.02	2.28
.320	372.42	370.14	2.28
.360	372.55	370.27	2.28
.400	372.67	370.40	2.27
.440	372.80	370.53	2.27
.480	372.92	370.66	2.26
.520	373.05	370.78	2.26
.560	373.17	370.91	2.26
.600	373.29	371.04	2.25
.640	373.41	371.17	2.25
.680	373.54	371.29	2.25
.720	373.66	371.42	2.24
.760	373.78	371.54	2.24
.800	373.90	371.67	2.23
.840	374.03	371.80	2.23
.880	374.15	371.92	2.23
.920	374.27	372.05	2.22
.960	374.39	372.17	2.22
1.000	374.51	372.30	2.21
1.040	374.63	372.42	2.21
1.080	374.75	372.55	2.21
1.120	374.87	372.67	2.20
1.160	374.99	372.79	2.20
1.200	375.11	372.92	2.20
1.240	375.23	373.04	2.19
1.280	375.35	373.16	2.19
1.320	375.47	373.29	2.18
1.360	375.59	373.41	2.18
1.400	375.71	373.53	2.18
1.440	375.83	373.65	2.17
1.480	375.94	373.77	2.17
1.520	376.06	373.90	2.16
1.560	376.18	374.02	2.16
1.600	376.30	374.14	2.16
1.640	376.41	374.26	2.15
1.680	376.53	374.38	2.15
1.720	376.65	374.50	2.15
1.760	376.76	374.62	2.14
1.800	376.88	374.74	2.14
1.840	377.00	374.86	2.13

```
                  ****************************************
                  *                                      *
                  *             SIMULATION               *
                  *                                      *
                  *            RUN P0880322              *
                  *                                      *
                  ****************************************

   ******************************
       SIMULATION CONDITIONS
   ******************************

           Total pressure: 34.0 atm
     Reactant temperature: 370.0 C
            Reactant flow:  3.31 l/min
                    H2/CO:  .81
      Coolant temperature: 370.0 C
             Coolant flow: 16.6 kg/hr
            Test duration: 200 min
           Time on stream: 97.9 hr

   ************************
     ESTIMATED PARAMETERS
   ************************

          Enthalpy of reaction: -59046.4 Kcal/Kmol
         Preexponential factor:  6.85
     Heat transfer coefficient: 464.1 Kcal/m**2*h*K

   ***************
       RESULTS
   ***************

      Final product temperature: 377.09 C
             Final product flow:  2.65 l/min
      Final coolant temperature: 376.23 C

                  CO conversion: 37.4 %
                  H2 conversion: 25.5 %

           Product distribution:      CO2    69.4
                                      H2O     1.8
                                      HC     28.3
                                      CH3OH    .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	371.62	370.18	1.45
.080	371.78	370.36	1.42
.120	371.93	370.54	1.39
.160	372.08	370.72	1.36
.200	372.23	370.89	1.34
.240	372.38	371.06	1.32
.280	372.52	371.23	1.30
.320	372.67	371.39	1.27
.360	372.81	371.55	1.25
.400	372.95	371.71	1.23
.440	373.09	371.87	1.22
.480	373.22	372.02	1.20
.520	373.36	372.18	1.18
.560	373.49	372.32	1.17
.600	373.62	372.47	1.15
.640	373.75	372.62	1.13
.680	373.88	372.76	1.12
.720	374.01	372.90	1.11
.760	374.13	373.04	1.09
.800	374.26	373.18	1.08
.840	374.38	373.31	1.07
.880	374.50	373.44	1.06
.920	374.62	373.58	1.04
.960	374.74	373.70	1.03
1.000	374.85	373.83	1.02
1.040	374.97	373.96	1.01
1.080	375.08	374.08	1.00
1.120	375.20	374.21	.99
1.160	375.31	374.33	.98
1.200	375.42	374.45	.97
1.240	375.53	374.57	.96
1.280	375.64	374.68	.95
1.320	375.75	374.80	.95
1.360	375.85	374.91	.94
1.400	375.96	375.03	.93
1.440	376.06	375.14	.92
1.480	376.16	375.25	.92
1.520	376.27	375.36	.91
1.560	376.37	375.46	.90
1.600	376.47	375.57	.90
1.640	376.57	375.67	.89
1.680	376.66	375.78	.89
1.720	376.76	375.88	.88
1.760	376.86	375.98	.87
1.800	376.95	376.08	.87
1.840	377.04	376.18	.87

```
                    ****************************************
                    *                                      *
                    *              SIMULATION              *
                    *                                      *
                    *            RUN P0880323              *
                    *                                      *
                    ****************************************

    ******************************
       SIMULATION CONDITIONS
    ******************************

          Total pressure: 34.0 atm
    Reactant temperature: 355.5 C
           Reactant flow:  6.16 l/min
                  H2/CO:   .88
     Coolant temperature: 355.5 C
            Coolant flow: 16.6 kg/hr
           Test duration: 180 min
          Time on stream: 103. hr

    ************************
     ESTIMATED PARAMETERS
    ************************

          Enthalpy of reaction: -53652.6 Kcal/Kmol
         Preexponential factor:  7.54
     Heat transfer coefficient: 483.8 Kcal/m**2*h*K

    ***************
       RESULTS
    ***************

     Final product temperature: 361.07 C
            Final product flow:  5.60 l/min
     Final coolant temperature: 360.35 C

                 CO conversion: 17.8 %
                 H2 conversion: 11.2 %

          Product distribution:      CO2    71.8
                                     H2O     1.6
                                     HC     25.6
                                     CH3OH   1.0
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	356.44	355.60	.84
.080	356.55	355.72	.83
.120	356.66	355.83	.83
.160	356.77	355.94	.83
.200	356.88	356.05	.83
.240	356.99	356.16	.82
.280	357.10	356.28	.82
.320	357.20	356.39	.82
.360	357.31	356.50	.81
.400	357.42	356.61	.81
.440	357.52	356.71	.81
.480	357.63	356.82	.81
.520	357.74	356.93	.80
.560	357.84	357.04	.80
.600	357.95	357.15	.80
.640	358.05	357.25	.80
.680	358.15	357.36	.79
.720	358.26	357.47	.79
.760	358.36	357.57	.79
.800	358.46	357.68	.79
.840	358.57	357.78	.78
.880	358.67	357.89	.78
.920	358.77	357.99	.78
.960	358.87	358.10	.78
1.000	358.97	358.20	.77
1.040	359.08	358.31	.77
1.080	359.18	358.41	.77
1.120	359.28	358.51	.77
1.160	359.38	358.61	.76
1.200	359.48	358.71	.76
1.240	359.57	358.82	.76
1.280	359.67	358.92	.76
1.320	359.77	359.02	.75
1.360	359.87	359.12	.75
1.400	359.97	359.22	.75
1.440	360.07	359.32	.75
1.480	360.16	359.42	.74
1.520	360.26	359.52	.74
1.560	360.36	359.62	.74
1.600	360.45	359.71	.74
1.640	360.55	359.81	.74
1.680	360.64	359.91	.73
1.720	360.74	360.01	.73
1.760	360.83	360.10	.73
1.800	360.93	360.20	.73
1.840	361.02	360.30	.72

```
                ************************************
                *                                  *
                *            SIMULATION            *
                *                                  *
                *           RUN P0880325           *
                *                                  *
                ************************************

****************************
   SIMULATION CONDITIONS
****************************

        Total pressure: 34.0 atm
  Reactant temperature: 369.9 C
         Reactant flow:  3.33 l/min
                H2/CO:  .85
   Coolant temperature: 369.9 C
          Coolant flow:  8.2 kg/hr
         Test duration: 170 min
        Time on stream: 109. hr

**********************
 ESTIMATED PARAMETERS
**********************

      Enthalpy of reaction: -41491.0 Kcal/Kmol
     Preexponential factor:  2.50
  Heat transfer coefficient:  51.3 Kcal/m**2*h*K

**************
   RESULTS
**************

  Final product temperature: 377.38 C
         Final product flow:  3.01 l/min
  Final coolant temperature: 374.37 C

             CO conversion: 18.6 %
             H2 conversion: 12.0 %

      Product distribution:      CO2    70.2
                                 H2O     1.8
                                 HC     27.6
                                 CH3OH    .4
```

TEMPERATURE PROFILES

z	T	Tc	T-Tc
.040	373.32	369.96	3.36
.080	373.86	370.07	3.79
.120	374.00	370.18	3.82
.160	374.09	370.29	3.80
.200	374.18	370.40	3.78
.240	374.26	370.51	3.75
.280	374.34	370.61	3.73
.320	374.42	370.72	3.70
.360	374.51	370.83	3.68
.400	374.59	370.93	3.66
.440	374.67	371.04	3.63
.480	374.75	371.14	3.61
.520	374.83	371.24	3.59
.560	374.91	371.35	3.57
.600	374.99	371.45	3.55
.640	375.07	371.55	3.52
.680	375.15	371.65	3.50
.720	375.23	371.75	3.48
.760	375.31	371.85	3.46
.800	375.39	371.95	3.44
.840	375.47	372.05	3.42
.880	375.55	372.14	3.40
.920	375.63	372.24	3.39
.960	375.70	372.34	3.37
1.000	375.78	372.43	3.35
1.040	375.86	372.53	3.33
1.080	375.94	372.62	3.31
1.120	376.01	372.72	3.30
1.160	376.09	372.81	3.28
1.200	376.17	372.90	3.26
1.240	376.24	373.00	3.24
1.280	376.32	373.09	3.23
1.320	376.39	373.18	3.21
1.360	376.47	373.27	3.20
1.400	376.54	373.36	3.18
1.440	376.62	373.45	3.16
1.480	376.69	373.54	3.15
1.520	376.77	373.63	3.13
1.560	376.84	373.72	3.12
1.600	376.91	373.81	3.10
1.640	376.99	373.90	3.09
1.680	377.06	373.99	3.07
1.720	377.13	374.07	3.06
1.760	377.20	374.16	3.04
1.800	377.28	374.25	3.03
1.840	377.35	374.33	3.02

Appendix M

Computer programs (PO reactor).

```
   n7x,1,s
   iles 0,1
      program pordat
   *************************************************************************
     This program stores in a file tcdpo'date'.dat run conditions and
     peak area of the TCD analysis of the content of 1 ml injection
     on the PORAPAK Q packed column.
    ************************************************************************

      character*18 OUTPUTFILE
      integer TIME, N
      real MFCCO, MFCH2, FRINCO, FRINH2, FROUT, CFR, H2BYP
      real H2, COBYP, CO, CH4, CO2, C2OL, C2PAR, H2O, C3OL
      real C3PAR, METOH, C4, C5PLUS, LIQHCW, AF, AAF, P, T

     a input

      call fparm(outputfile)
      open (10,file = outputfile)
      write(1,*) 'Enter in the same order:'
      write(1,*)
      write(1,*) '- Run duration(min)(TIME)'
      write(1,*) '- Pressure(psig)(P),Bed Temperature(oC)(T)'
      write(1,*) '  MFC indication (MFC) MFCCO and MFCH2'
      write(1,*) '- FlowCO in (FRINCO),FlowH2 in (FRINH2)'
      write(1,*) '- Flow out (FROUT) (ml STP/min)'
      write(1,*) '- Coolant flow rate (CFR) (kg/hr)'
      write(1,*) '- H2 peak area corresponding to peak area for bypass '
      write(1,*) '  and reactor injections (H2BYP and H2)'
      write(1,*) '- CO peak area for bypass and reactor loop injection:'
      write(1,*) '  COBYP AND CO '
      write(1,*) '- Peak area for CH4,CO2,C2=,C2,H2O,C3=,C3,CH3OH,C4s,'
      write(1,*) '  C5+'
      write(1,*) '- Weight of liquid hydrocarbon (LIQHCW)'
      write(1,*) '- Weight of aqueous fraction (AF)'
      write(1,*) '- Pourcentage of methanol in aqueous fraction (AAF)'
      write(1,*) '- Number of compounds in the hydrocarbons (N)'
c
      read(1,*) TIME ,P ,T ,MFCCO,MFCH2,FRINCO ,FRINH2,
     $          FROUT , CFR, H2BYP ,H2 ,
     $          COBYP ,CO ,
     $          CH4 ,CO2 ,C2OL ,C2PAR ,H2O ,C3OL ,C3PAR ,
     $          METOH ,C4 ,C5PLUS, LIQHCW, AF, AAF, N
c
      write(10,*) TIME ,P ,T ,MFCCO,MFCH2, FRINCO, FRINH2,
     $            FROUT ,CFR ,H2BYP ,H2 ,
     $            COBYP ,CO ,
     $            CH4 ,CO2 ,C2OL ,C2PAR ,H2O ,C3OL ,C3PAR ,
     $            METOH ,C4 ,C5PLUS, LIQHCW, AF, AAF, N
      close(10)
c
      stop
      end
```

```
ftn7x,1,s
$files 0,1
$CDS ON
      SUBROUTINE PORPRO (TIME,P,T,MFCCO,MFCH2,FRINCO,FRINH2,FROUT,CFR,
     $                  H2BYP,H2,COBYP,CO,TCDMASS,VLOOP,VLOOPB,WHSV,
     $                  REST,MCAT,H2PC,COPC,FRINT,LIQHCW,AF,AAF)
c
c***********************************************************************
c   This program calculates the TCD analysis of 1 ml GC gas injection
c   coming from non-condensed fraction of the Pseudoadiabatic Reactor.
c***********************************************************************
c
      real TIME,COPC,H2PC,P,T,FRINCO,FRINH2,FROUT,FRINT,CFR,H2BYP,H2
      real COBYP,CO,CH4,CO2,C2OL,C2PAR,H2O,C3OL,C3PAR,C4,C5PLUS,FLOW
      real H2CONV,COCONV,MFCH2,MFCCO,METOH,MCAT,LIQHCW,AF,AAF,REST
      real VLOOP,VLOOPB
      dimension tcdmass(12)
      character*1 R,R1
      character*18 DATAFILE
      character*10 NUM,SRN*15
c
c***********************************************************************
c                             Data input
c***********************************************************************
c
      write(1,*) 'Enter datafile number.'
      write(1,*) '  Ex. : for run sept. the 10th 1987 : 100987'
      read(1,'(A10)') NUM
      IEND = index(NUM,' ')
      SRN = NUM(1:IEND-1) // '.DAT '
      DATAFILE = 'POR' // SRN
c
      open (10,file = DATAFILE)
      read(10,*) TIME,P,T,MFCCO,MFCH2,
     $           FRINCO,FRINH2,FROUT,CFR,H2BYP,H2,
     $           COBYP,CO,
     $           CH4,CO2,C2OL,C2PAR,H2O,C3OL,C3PAR,
     $           METOH,C4,C5PLUS,LIQHCW,AF,AAF,N
      close(10)
      write(1,*) ' !!!!Datafile read !!!! '
c
c**********************************************************************
c                             Calculations
c**********************************************************************
c
      MCAT = 550
      COPC = FRINCO/(FRINCO+FRINH2)*100
      H2PC = 100 - COPC
      FRINT = FRINCO + FRINH2
      WHSV = ((FRINCO/24.2*28)+(FRINH2/24.2*2))/MCAT*60
      REST = 0.687 / FRINT *60 *P/14.7 *273/(T +273)
c
      H2 = H2CAL( H2)
      H2BYP = H2CAL ( H2BYP)
      CO = COCAL ( CO)
      COBYP = COCAL ( COBYP)
c
      TCDMASS(1) = 2*H2/24.2
      TCDMASS(2) = 28*CO/24.2
      TCDMASS(3) = CO2/1200
      TCDMASS(4) = (.6E-3*H2O - .6)
      TCDMASS(5) = METOH/1580
      TCDMASS(6) = CH4/ 2080.
      TCDMASS(7) = C2OL/ 1800.
      TCDMASS(8) = C2PAR/ 1800.
      TCDMASS(9) = C3OL/ 1538.
      TCDMASS(10) = C3PAR/ 1615.
      TCDMASS(11) = C4/ 1666.
      TCDMASS(12) = C5PLUS/ 1600.
c
      VLOOP =TCDMASS(1)/2 + TCDMASS(2)/28 + TCDMASS(3)/44 +
     $          TCDMASS(4)/18 + TCDMASS(5)/32 + TCDMASS(6)/16 +
     $          TCDMASS(7)/28 + TCDMASS(8)/30 + TCDMASS(9)/42 +
     $          TCDMASS(10)/44 + TCDMASS(11)/58 + TCDMASS(12)/80
      VLOOP = VLOOP*24.2
      VLOOPB = H2BYP + COBYP

      end
c**********************************************************************
c Calibration function to compute H2 volume (ul) from the TCD peak area
c         Calibration Date : Jan. 88
c         Valid for the Area range (Range set at 2^0 on HP5890A) :
c            3300 (100 ulSTP) to 122000 (1000 ulSTP)
c***********************************************************************
c
      FUNCTION H2CAL(X)
      H2CAL = 63.184 + .01217628*X - 8.75560127512E-08 * X**2
     $                             + 6.67971183518E-13 * X**3
     $                             - 2.05991445345E-18 * X**4
      return
      end
c***********************************************************************
c Calibration Function to compute CO volume (ul) from the TCD peak area
c          Calibration Date : Jan. 88
c          Valid for the area range (range set at 2^0 on HP5890A):
c            88000 (50ulSTP) to 1.65E+6 (1000 ulSTP)
c***********************************************************************
c
      FUNCTION COCAL(X)
      COCAL = -7.821 + .000630125*X - 1.79924571963E-10 * X**2
     $                              + 2.12702430797E-16 * X**3
     $                              - 6.14736379050E-23 * X**4
      return
      end
```

```
ftn 7x,1,s
$files 0,8
$cds on
      PROGRAM POPROD
C**************************************************************************
C
C        CALCULATION OF WEIGHT AND MOLAR DISTRIBUTIONS OF THE
C        PRODUCTS FOR THE CONVERSION OF SYNTHETIC GAS TO HYDROCARBONS
C        FOR THE PSEUDOADIABATIC REACTOR
C
C**************************************************************************
C
      CHARACTER*10 RN ,SRN*15
      CHARACTER*6 PORPRO
      CHARACTER *16 POGHC,LIQCOMP,extent
      REAL WLHC(200),THC(200),TCD(200),HCM(200),MYDDG(200)
      REAL MTDDL(200),MTDDA(200),MTDD(200),PMTDD(200),PTHC(200)
      REAL TDD(200),GHC(200),MTDDG(200)
      REAL SLLHC(20),SC5P(20),C5P(70)
      INTEGER PM(200),CN(200), NH(200),OPTION, LUARY(1), NUMLUS
      REAL P,T,TIME,MFCCO,MFCH2,MCAT,MT,RH2CO,MTDDX
      REAL LLHC(70),LTHC(15),METOH(10), TCDMASS(12)
      REAL MET,METM,METOHB,MBO,MBC,MBT,LIQM,LIQHCW,LAR,NCM
      REAL MBOPC,MBCPC,MBHPC,AAF,AF,WAT
      REAL TCDHC,STCD,CORR,C1COR,C2COR,C3COR,WM,WW,MT1,TT,MTT
      REAL COCONV,H2CONV,MOC,MOP,PMO,MCP1,MCP2,MCL1,MCL2,MCP
      REAL PMC,MHC,MHP1,MHP2,MHL1,MHL2,MHP,PMH,MTC,MTP,PMT,MCC
      REAL FRINCO,FRINH2,FROUT,CFR,COPC,H2PC,WHSV
      REAL REST,VLOOP,VLOOPB,TP5,TP2
      REAL MTDDG,MTDD
      CHARACTER NAME(170)*50,LNAME(12)*40,LHCNAME(50)*30,LLNAME(13)*40
      DATA (LNAME(I), I=6,12) /'i-Butane','n-Butane','Butenes',
     $'Paraffins + Cycloparaffins','Olefins + Cycloolefins',
     $'Aromatics','C11+'/
      DATA LLNAME /'C5-C8 Paraffins + Cycloparaffins',
     $'C5-C8 Olefins + Cycloolefins','C9+ P+O+N','Benzene','Toluene',
     $'C8 Aromatics','C9 Aromatics','C10 Aromatics','C11 Aromatics',
     $'C12 Aromatics','C13 Aromatics','C14 Aromatics','C15 Aromatics'/
C
C*************************************************************************
C
C                             DATA TRANSFER
C
C*************************************************************************
C
      N=159
      WRITE(1,*)'ENTER  RUN IDENTIFICATION'
      WRITE(1,*)'Ex. : for the run conducted the 10th of Marsh 1988'
      WRITE(1,*)'      enter 880310  '
      READ(1,'(A6)') RN
      IEND = INDEX(RN,' ')
      SRN = RN(1:IEND-1) // '.DAT'
      POGHC = 'POG' // SRN
      LIQCOMP = 'POL' // SRN
      OPEN(10,FILE='POMOLEWEIGHT.DAT')
      READ(10,*) (PM(I), I=1,N)
      CLOSE (10)
      write (1,*) 'First file OK !'
      OPEN (20, FILE = 'POPRODNAME.DAT')
      READ (20,*) (NAME(I), I=1,N)
      CLOSE (20)
      write (1,*) 'Second file OK'
      OPEN (30, FILE = 'POCNUM.DAT')
      READ (30,*) (CN(I), I=1,N)
      CLOSE (30)
      write (1,*) 'Third file OK !'
      OPEN (40, FILE = POGHC)
      READ (40,*) (GHC(I), I=1,N)
      CLOSE (40)
      write (1,*) 'Fourth file OK !'
      OPEN (50, FILE = LIQCOMP)
      READ (50,*) (WLHC(I), I=1,N)
      CLOSE (50)
      write (1,*) 'Fifth file OK !'
      OPEN (65, FILE = 'POLUMPNAME.DAT')
      READ (65,*) (LHCNAME(I), I=1,50)
      CLOSE (65)
      write (1,*) 'Sixth file OK!'
C
C***********************************************************************
C          OUTPUT ADDRESS FOR RESULT PRINTING
C***********************************************************************
C
      Write(1,*) 'Enter output adress for result printing: '
      write(1,*) '     Screen: 1 ; Printer: 6    '
      Read (1,*) NO
C
C***********************************************************************
C        LOCKING THE PRINTER (IO 6) TO AVOID ANY PRINTING INTERFERENCE
C           FROM OTHER USERS WHILE PRINTING THE RESULTS
C***********************************************************************
C
c     if ( NO .eq. 6 ) then
c         OPTION = 040001B
c         LUARY(1) = NO
c         NUMLUS = 1
c         CALL LURQ (OPTION, LUARY , NUMLUS)
c     END IF
C
C***********************************************************************
      WRITE (NO,70) RN
   70 FORMAT(1X,18X,40'*',/,1X,18X,'*',38X,'*',/,
     $       1X,18X,'*',5X,'SYNTHESIS GAS CONVERSION RUN',5X,'*',/,
     $       1X,18X,'*',38X,'*',/,
     $       1X,18X,'*',14X,'PO',A8,14X,'*',/,1X,18X,'*',38X,'*',/,
     $       1X,18X,40'*',/)
C
C***********************************************************************
C         PRELIMINARY CALCULATIONS FROM THE TCD ANALYSIS
C***********************************************************************
```

```
C
C<<<<<<<<< Conversions & Product distributions for the analysis >>>>>>>

      CALL PORPRO(time,p,t,mfcco,mfch2,frinco,frinh2,frout,cfr,h2byp
     $            ,h2,cobyp,co,tcdmass,vloop,vloopb,whsv,rest,mcat,
     $            h2pc,copc,frint,liqhcw,af,aaf)
C
C***********************************************************************
C          CORRECTION OF THE INPUT FILES (GHC,WLHC)
C***********************************************************************
C
      TC1=0
      TC2=0
      DO i=1,N
      TC1 = TC1 + GHC(i)
      TC2 = TC2 + WLHC(i)
      ENDDO
      DO i=1,N
      GHC(i) = GHC(i)/TC1*100
      WLHC(i) = WLHC(i)/TC2*100
      ENDDO
C
C***********************************************************************
C                  TOTAL DISTRIBUTION OF NON-CONDENDED GAS
C   Corrected from the TCD analysis for the products non detected
C   by the TCD detector
C***********************************************************************
C
      TCDHC = 0.0
      STCD = 0.0
      DO i = 1,12
      TCD(i) =  TCDMASS(i)
      STCD = STCD + TCD(i)
      ENDDO
      DO i = 1,12
      TCD(i) = 100.*TCD(i) / STCD
      ENDDO
      TCDHC = 0.
      DO I=6,12
      TCDHC = TCDHC + TCD(I)
      ENDDO
      C1COR = 100.*TCD(6)/GHC(1) - TCDHC
      C2COR = 100.*(TCD(7) + TCD(8))/(GHC(2) + GHC(3)) - TCDHC
      C3COR = 100.*(TCD(9) + TCD(10))/(GHC(4) + GHC(5)) - TCDHC
      WRITE (1,*) 'HC WEIGHT TO BE ADDED TO 100 GRAMS OF PRODUCTS '
      WRITE (1,*) 'DETECTED BY TCD,CALCULATED WITH C1,C2,C3 :'
      WRITE (1,*) C1COR,C2COR,C3COR
      WRITE (1,*) 'ENTER HC CORRECTION MASS FOR TCD ANALYSIS ON '
      WRITE (1,*) 'A 100 GRAMS BASIS OF ALL DETECTED PRODUCTS'
      READ (1,*) CORR
      DO I=1,5
      TCD(I) = TCD(I)/(1+.01*CORR)
      END DO
      HC = (TCDHC +CORR)/(1+.01*CORR)
C
```

```
C***********************************************************************
C                              AQUEOUS FRACTION
C***********************************************************************
C
      IF (AAF.GT.0.0) GOTO 200
      IF (AF.GT.0.0) GOTO 220
      WM=0.
      WW=0.
      GOTO 230
  200 WM=(1.039*AAF) + 0.0925
  220 WW=100-WM
  230 MET=WM*AF/100
      WAT=AF-MET
C
C***********************************************************************
C                  MASS DISTRIBUTION OF NON-CONDENSED GAS
C***********************************************************************
C
      DO I=1,5
      TCD(I) = TCD(I)/100
      END DO
      DO I=1,N
      TCD(I+5) = GHC(I)*(HC/100)/100
      END DO
C
C***********************************************************************
C                  MOLAR DISTRIBUTION OF NON-CONDENSED GAS
C***********************************************************************
C
      MT1 =0.0
      TT = 0.0
      MT1 = TCD(1)/2 + TCD(2)/28 + TCD(3)/44 + TCD(4)/18 + TCD(5)/32
      DO I=6,N+5
      HCM(I) = TCD(I)/PM(I-5)
      TT = TT + HCM(i)
      ENDDO
      MTT = MT1 + TT
      HCM(1) = TCD(1)/2/MTT
      HCM(2) = TCD(2)/28/MTT
      HCM(3) = TCD(3)/44/MTT
      HCM(4) = TCD(4)/18/MTT
      HCM(5) = TCD(5)/32/MTT
      DO I=1,N
      HCM(I+5) = TCD(I+5)/PM(I)/MTT
      END DO
C
C***********************************************************************
C                              CONVERSIONS
C***********************************************************************
C
      COCONV = 100*((COPC*FRINT/100)-(HCM(2)*FROUT))/(COPC*FRINT/100)
      H2CONV = 100*((H2PC*FRINT/100)-(HCM(1)*FROUT))/(H2PC*FRINT/100)
C
C***********************************************************************
C                         MASS BALANCES (ugram/sec)
```

```
C**********************************************************************
C
      MCP2 = 0.0
      MCL2 = 0.0
      MHP2 = 0.0
      MHL2 = 0.0
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Oxygen >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C
C----------- CONVERTED OXYGEN -----------------------
      MOC = FRINCO*TIME/24.2*16
C----------- IN PRODUCT -----------------------------
      MOP = HCM(3)*FROUT*TIME/24.2*32 + HCM(4)*FROUT*TIME/24.2*16 +
     $      HCM(5)*FROUT*TIME/24.2*16 + MET/32*16 + WAT/18*16 +
     $      HCM(2)*FROUT*TIME/24.2*16
      PMO = (MOC-MOP)/MOC *100
C
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Carbon >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C
      MCC = FRINCO*TIME/24.2*12
C----------- IN GAS----------------------------------
      MCP1 = HCM(3)*FROUT*TIME/24.2*12 + HCM(2)*FROUT*TIME/24.2*12
      DO I=6,N+6
      MCP2 = MCP2 + (HCM(I)*FROUT*TIME/24.2)*12*CN(I-5)
      END DO
C----------- IN LIQUID ------------------------------
      MCL1 = MET/32*12
      DO I=1,N
      MCL2 = MCL2 + (WLHC(I)*LIQHCW/PM(I)*CN(I)*12/100)
      END DO
C----------- TOTAL ----------------------------------
      MCP = MCP1 + MCP2 + MCL1 + MCL2
      PMC = (MCC-MCP)/MCC *100
C
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Hydrogen >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C
C----------- CALCULATION OF NH(I) -------------------
      DO I=1,N
      NH(I) = PM(I)-(CN(I)*12)
      END DO
C----------- CONVERTED HYDROGEN ---------------------
      MHC = FRINH2*TIME/24.2*2
C----------- IN GAS ---------------------------------
      MHP1 = HCM(4)*FROUT*TIME/24.2*2 + HCM(5)*FROUT*TIME/24.2*4 +
     $      HCM(1)*FROUT*TIME/24.2*2
      DO I=6,N+6
      MHP2 = MHP2 + (HCM(I)*FROUT*TIME/24.2*NH(I-5))
      END DO
C----------- IN LIQUID ------------------------------
      MHL1 = MET/32*4 + WAT/18*2
      DO I=1,N
      MHL2 = MHL2 + (WLHC(I)*LIQHCW/PM(I)*NH(I)/100)
      END DO
C----------- TOTAL ----------------------------------
      MHP = MHP1 + MHP2 + MHL1 + MHL2
      PMH = (MHC-MHP)/MHC *100
```

```
C<<<<<<<<<<<<<<<<<<<<<<<<<<<<< Total >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>

      MTC = MCC + MHC + MOC
      MTP = MCP + MHP + MOP
      PMT = (MTC-MTP)/MTC *100
C
C***********************************************************************
C                    TOTAL PRODUCT DISTRIBUTION
C***********************************************************************
C
      MTDDX = 0.0
      TP5 = 0.0
      TP2 = 0.0
      MTDDG(1) = HCM(1)*FROUT*TIME/24.2*2
      MTDDG(2) = HCM(2)*FROUT*TIME/24.2*28
      MTDDG(3) = HCM(3)*FROUT*TIME/24.2*44
      MTDDG(4) = HCM(4)*FROUT*TIME/24.2*18
      MTDDG(5) = HCM(5)*FROUT*TIME/24.2*32
      DO I=6,N+5
      MTDDG(I) = HCM(I)*FROUT*TIME/24.2*PM(I-5)
      END DO
      DO I=1,N
      MTDDL(I+5) = WLHC(I)*LIQHCW/100
      END DO
      MTDDL(4) = WAT
      MTDDL(5) = MET
      DO I=1,N+5
      MTDD(I) = MTDDG(I) + MTDDL(I)
      MTDDX = MTDDX + MTDD(I)
      END DO
      DO I=1,N+5
      PMTDD(I) = MTDD(I)/MTDDX*100
      END DO
      DO I=1,5
      TP5 = TP5 + PMTDD(I)
      END DO
      DO I=1,N
      THC(I) = PMTDD(I+5)/(1-(.01*TP5))
      END DO
      TP2 = PMTDD(1) + PMTDD(2)
      DO I=6,N+5
      PHC = PHC + (PMTDD(I)/(1-(.01*TP2)))
      ENDDO
      PCO2 = PMTDD(3)/(1-(.01*TP2))
      PH2O = PMTDD(4)/(1-(.01*TP2))
      PMETOH = PMTDD(5)/(1-(.01*TP2))
      RH2CO = FRINH2/FRINCO
      FL = FRINCO + FRINH2
      x3= hcm(3)*frout/24.2/1000*60
      xCO=frinco*coconv/100/24.2/1000*60
      x1=xCO-x3
      x2=(hcm(5)+hcm(3))*frout/24.2/1000*60
c
C**********************************************************************
```

```
C                        OUTPUT FILE
C***********************************************************************
C
      extent= 'pom' // srn
      OPEN(70,FILE = 'extent')
      WRITE(70,*) X1,X2,X3
      CLOSE(70)
C
C***********************************************************************
C                      RESULT PRINTING
C***********************************************************************
C
      WRITE(NO,5)
    5 FORMAT(5X,28'*')
      WRITE(NO,10)
   10 FORMAT(5X,4X,'OPERATING CONDITIONS')
      WRITE(NO,15)
   15 FORMAT(5X,28'*',/)
      WRITE(NO,20) T
   20 FORMAT(11X,'TEMPERATURE: ',f5.1,1X,' C')
      P1=P/14.7
      WRITE(NO,25) P1
   25 FORMAT(14X,'PRESSURE: ',I3,1X,'atm')
      WRITE(NO,27) FL
   27 FORMAT(14X,'GAS FLOW: ',F5.2,1X,'l/min')
      WRITE(NO,30) REST
   30 FORMAT(8X,'RESIDENCE TIME: ',F5.1,1X,'s')
      WRITE(NO,35) RH2CO
   35 FORMAT(11X,'H2/CO ratio: ',F4.2)
      WRITE(NO,40) CFR
   40 FORMAT(10X,'COOLANT FLOW: ',F4.1,1X,'kg/hr')
      WRITE(NO,47) TIME
   47 FORMAT(9X,'TEST DURATION: ',F3.0,1X,'minutes',/)
      WRITE(NO,55)
   55 FORMAT(5X,20'*')
      WRITE(NO,60)
   60 FORMAT(9X,'CONVERSIONS')
      WRITE(NO,65)
   65 FORMAT(5X,20'*',/)
      WRITE(NO,68) COCONV
   68 FORMAT(7X,'CO CONVERSION: ',F4.1,1X,'%')
      WRITE(NO,75) H2CONV
   75 FORMAT(7X,'H2 CONVERSION: ',F4.1,1X,'%',/)
      WRITE(NO,77)
   77 FORMAT(5X,28'*')
      WRITE(NO,78)
   78 FORMAT(9X,'PRODUCT DISTRIBUTION')
      WRITE(NO,79)
   79 FORMAT(5X,28'*',/)
      WRITE(NO,80) LIQHCW
   80 FORMAT(7X,'           MASS OF GASOLINE:  ',F6.2,1X,'g',/)
      WRITE(NO,85) AF
   85 FORMAT(7X,'      MASS OF AQUEOUS PHASE:  ',F6.2,1X,'g')
      WRITE(NO,90) WW
   90 FORMAT(7X,'          COMPOSITION (WT%):  ',F6.2,1X,'% WATER')
```

```
      WRITE(NO,95) WM
   95 FORMAT(36X,F6.2,1X,'% METHANOL',/)
      WRITE(NO,100)
  100 FORMAT(7X,'PRODUCT MASS DISTRIBUTION (WT%):',/)
      WRITE(NO,105) PCO2
  105 FORMAT(18X,'CO2      ',F5.2)
      WRITE(NO,110) PH2O
  110 FORMAT(18X,'H2O      ',F5.2)
      WRITE(NO,115) PHC
  115 FORMAT(18X,'HC       ',F5.2)
      WRITE(NO,120) PMETOH
  120 FORMAT(18X,'METOH    ',F5.2,/)
      WRITE(NO,121)
  121 FORMAT(5X,23'*')
      WRITE(NO,125)
  125 FORMAT(10X,'MASS BALANCE')
      WRITE(NO,127)
  127 FORMAT(5X,23'*',/)
      WRITE(NO,128)
  128 FORMAT(21X,'    IN (g)    ',3X,'OUT (g)  ',4X,'%ERROR',/)
      WRITE(NO,130) MCC,MCP,PMC
  130 FORMAT(12X,'CARBON:',4X,F7.2,6X,F7.2,6X,F7.2)
      WRITE(NO,131) MHC,MHP,PMH
  131 FORMAT(10X,'HYDROGEN:',4X,F7.2,6X,F7.2,6X,F7.2)
      WRITE(NO,132) MOC,MOP,PMO
  132 FORMAT(12X,'OXYGEN:',4X,F7.2,6X,F7.2,6X,F7.2,/)
      WRITE(NO,133) MTC,MTP,PMT
  133 FORMAT(13X,'TOTAL:',4X,F7.2,6X,F7.2,6X,F7.2,/)
C     WRITE(NO,135)
C 135 FORMAT(5X,30'*',/)
C     WRITE(NO,140)
C 140 FORMAT(11X,'VOLUME INJECTION',/)
C     WRITE(NO,145)
C 145 FORMAT(5X,30'*',/)
C     WRITE(NO,150) VLOOP
C 150 FORMAT(7X,'NON-CONDENSED GAS LOOP :',2X,F4.1,2X,'ul',/)
C     WRITE(NO,155) VLOOPB
C 155 FORMAT(7X,'        BYPASS GAS LOOP :',2X,F4.1,2X,'ul',/)
C
      Write(1,*) 'Enter Output Adress for Hydrocarbon Distributions:'
      Write(1,*) '  Screen :1 ; Printer :6 '
      Read (1,*) NO
      WRITE(NO,640)
C
  640 FORMAT(//////,21X,5'*','HYDROCARBON DISTRIBUTION',
     $5'*',//)
C
C<<<<< LIQUID,GAS AND TOTAL HYDROCARBON MASS PRODUCT DISTRIBUTIONS >>>>>
      WRITE(NO,671)
  671 FORMAT(//,6X,3'*','LIQUID,GAS AND TOTAL HYDROCARBON MASS DISTRIBUT
     $IONS',3'*',//)
      WRITE(NO,672)
  672 FORMAT(1X,'NUMBER',13X,'NAME',12X,'LIQ HC %',2X,'GASEOUS HC %',
     $2X,'TOTAL HC %',//)
      DO I=1,N
      WRITE(NO,674) I,NAME(I),WLHC(I),GHC(I),THC(I)
      END DO
  674 FORMAT(1X,I3,1X,A31,1X,F6.3,5X,F6.3,6X,F6.3)
C***********************************************************************
C           LUMPED C5+ TOTAL AND LIQUID HYDROCARBON COMPOSITIONS
C***********************************************************************
      LLHC(1)= WLHC(15)
      C5P(1) = THC(15)
      LLHC(2)= WLHC(12)
      C5P(2) = THC(12)
      LLHC(3)= WLHC(14)+WLHC(16)+WLHC(17)+WLHC(18)
      C5P(3) = THC(14) +THC(16) +THC(17) +THC(18)
      LLHC(4)= WLHC(13)
      C5P(4) = THC(13)
      LLHC(5)= WLHC(24)
      C5P(5) = THC(24)
      LLHC(6)= WLHC(19)+WLHC(21)+WLHC(22)
      C5P(6) = THC(19) +THC(21) +THC(22)
      LLHC(7)= WLHC(20)
      C5P(7) = THC(20)
      LLHC(8)= WLHC(23)+WLHC(31)
      C5P(8) = THC(23) +THC(31)
      DO I=25,29
      LLHC(8)= LLHC(8)+WLHC(I)
      C5P(8) = C5P(8) +THC(I)
      END DO
      LLHC(9)= WLHC(34)
      C5P(9) = THC(34)
      LLHC(10)= WLHC(30)
      C5P(10) = THC(30)
      LLHC(11)= WLHC(32)
      C5P(11) = THC(32)
      LLHC(12)= 0.
      C5P(12) = 0.
      LLHC(13)= WLHC(35)+WLHC(36)
      C5P(13) = THC(35) +THC(36)
      LLHC(14)= 0.
      C5P(14) = 0.
      LLHC(15)= WLHC(37)+WLHC(38)+WLHC(39)+WLHC(41)+WLHC(42)
      C5P(15) = THC(37) +THC(38) +THC(39) +THC(41) +THC(42)
      LLHC(16)= WLHC(40)
      C5P(16) = THC(40)
      LLHC(17)= 0.
      C5P(17) = 0.
      LLHC(18)= WLHC(44)+WLHC(56)
      C5P(18) = THC(44) +THC(56)
      LLHC(19)= WLHC(49)+WLHC(50)+WLHC(51)
      C5P(19) = THC(49) +THC(50) +THC(51)
      LLHC(20)= WLHC(43)+WLHC(45)+WLHC(46)+WLHC(52)+WLHC(53)+WLHC(54)+
     $          WLHC(55)+WLHC(57)+WLHC(58)+WLHC(59)+WLHC(60)+WLHC(61)+
     $          WLHC(63)+WLHC(64)+WLHC(65)
      C5P(20) = THC(43)+THC(45)+THC(46)+THC(52)+THC(53)+THC(54)+THC(55)
     $ +THC(57)+THC(58)+THC(59)+THC(60)+THC(61)+THC(63)+THC(64)+THC(65)
      LLHC(21)= WLHC(47)+WLHC(62)+WLHC(66)+WLHC(67)+WLHC(68)
      C5P(21) = THC(47) +THC(62) +THC(66) +THC(67) +THC(68)
      LLHC(22)= WLHC(71)+WLHC(73)+WLHC(74)+WLHC(75)+WLHC(76)+WLHC(83)
      C5P(22) = THC(71) +THC(73) +THC(74) +THC(75) +THC(76) +THC(83)
      LLHC(23)= WLHC(33)
      C5P(23) = THC(33)
      LLHC(24)= WLHC(48)
      C5P(24) = THC(48)
      LLHC(25)= WLHC(69)
      C5P(25) = THC(69)
      LLHC(26)= WLHC(70)
      C5P(26) = THC(70)
      LLHC(27)= WLHC(72)
      C5P(27) = THC(72)
      LLHC(28)= WLHC(80)+WLHC(82)+WLHC(84)
      C5P(28) = THC(80) +THC(82) +THC(84)
      LLHC(29)= WLHC(78)+WLHC(79)+WLHC(81)
      C5P(29) = THC(78) +THC(79) +THC(81)
      LLHC(30)= WLHC(77)
      C5P(30) = THC(77)
      LLHC(31)= WLHC(87)+WLHC(89)
      C5P(31) = THC(87) +THC(89)
      LLHC(32)= WLHC(88)+WLHC(91)
      C5P(32) = THC(88) +THC(91)
      LLHC(33)= WLHC(90)+WLHC(92)+WLHC(94)+WLHC(95)+WLHC(96)
      C5P(33) = THC(90) +THC(92) +THC(94) +THC(95) +THC(96)
      LLHC(34)= WLHC(97)+WLHC(98)+WLHC(101)
      C5P(34) = THC(97) +THC(98) +THC(101)
      LLHC(35)= WLHC(85)
      C5P(35) = THC(85)
      LLHC(36)= WLHC(86)
      C5P(36) = THC(86)
      LLHC(37)= WLHC(93)+WLHC(99)+WLHC(100)
      C5P(37) = THC(93) +THC(99) +THC(100)
      LLHC(38)= WLHC(102)
      C5P(38) = THC(102)
      LLHC(39)= WLHC(103)+WLHC(104)+WLHC(105)+WLHC(109)+WLHC(110)+
     $          WLHC(111)+WLHC(113)+WLHC(119)
      C5P(39) = THC(103) +THC(104) +THC(105) +THC(109) +THC(110) +
     $          THC(111) +THC(113) +THC(119)
      LLHC(40)= WLHC(106)+WLHC(107)+WLHC(108)+WLHC(116)+WLHC(117)+
     $          WLHC(118)
      C5P(40) = THC(106) +THC(107) +THC(108) +THC(116) +THC(117) +
     $          THC(118)
      LLHC(41)= WLHC(120)+WLHC(121)
      C5P(41) = THC(120) +THC(121)
      LLHC(42)= WLHC(125)+WLHC(132)
      C5P(42) = THC(125) +THC(132)
      LLHC(43)= WLHC(123)
      C5P(43) = THC(123)
      LLHC(44)= WLHC(112)+WLHC(114)+WLHC(115)+WLHC(122)+WLHC(127)
      C5P(44) = THC(112) +THC(114) +THC(115) +THC(122) +THC(127)
      LLHC(45)= WLHC(128)+WLHC(129)+WLHC(130)
      C5P(45) = THC(128) +THC(129) +THC(130)
      LLHC(46)= WLHC(126)
      C5P(46) = THC(126)
      LLHC(47)= WLHC(124)+WLHC(133)
      C5P(47) = THC(124) +THC(133)
      LLHC(48)= WLHC(134)
      C5P(48) = THC(134)
      DO I=135,141
      LLHC(48)= LLHC(48)+WLHC(I)
      C5P(48) = C5P(48) +THC(I)
      END DO
      LLHC(49)= WLHC(142)
      C5P(49) = THC(142)
      DO I=143,149
      LLHC(49)= LLHC(49)+WLHC(I)
      C5P(49) = C5P(49) +THC(I)
      END DO
      LLHC(50)= WLHC(150)
      C5P(50) = THC(150)
      DO I=151,159
      LLHC(50)= LLHC(50)+WLHC(I)
      C5P(50) = C5P(50) +THC(I)
      END DO
C ************** C4- total & liquid hydrocarbon fractions*************
      WLHC4M = WLHC(1)
      THC4M = THC(1)
      DO I=2,11
      WLHC4M = WLHC4M + WLHC(I)
      THC4M = THC4M + THC(I)
      END DO
C***** Normalization C5+ total and liquid hydrocarbon distribution*****
      DO I=1,50
      LLHC(I)= 100*LLHC(I)/(100-WLHC4M)
      C5P(I) = 100*C5P(I)/(100-THC4M)
      END DO
C
C******SUMMARY OF C5+TOTAL & LIQUID HYDROCARBON LUMPED COMPOSITION********
C
      SLLHC(2)= LLHC(3)+LLHC(8)+LLHC(11)+LLHC(14)+LLHC(16)+LLHC(19)+
     $          LLHC(21)
      SC5P(2) = C5P(3) +C5P(8) +C5P(11) +C5P(14) +C5P(16) +C5P(19) +
     $          C5P(21)
      SLLHC(1)= -SLLHC(2)
      SC5P(1) = -SC5P(2)
      DO I=1,21
      SLLHC(1)= SLLHC(1) + LLHC(I)
      SC5P(1) = SC5P(1) + C5P(I)
      END DO
      SLLHC(3)= LLHC(22)
      SC5P(3) = C5P(22)
      SLLHC(4)= LLHC(23)
      SC5P(4) = C5P(23)
      SLLHC(5)= LLHC(24)
      SC5P(5) = C5P(24)
      SLLHC(6)= LLHC(25)+LLHC(26)+LLHC(27)
      SC5P(6) = C5P(25) +C5P(26) +C5P(27)
      SLLHC(7)= LLHC(28)+LLHC(29)+LLHC(30)+LLHC(35)+LLHC(36)
      SC5P(7) = C5P(28) +C5P(29) +C5P(30) +C5P(35) +C5P(36)
      SLLHC(8)= LLHC(31)+LLHC(32)+LLHC(33)+LLHC(34)+LLHC(37)+LLHC(38)
      SC5P(8) = C5P(31) +C5P(32) +C5P(33) +C5P(34) +C5P(37) +C5P(38)
      SLLHC(9)= LLHC(39)+LLHC(40)+LLHC(41)
      SC5P(9) = C5P(39) +C5P(40) +C5P(41)
      SLLHC(10)= LLHC(42)+LLHC(43)+LLHC(44)+LLHC(45)
      SC5P(10) = C5P(42) +C5P(43) +C5P(44) +C5P(45)
      SLLHC(11)= LLHC(46)+LLHC(47)+LLHC(48)
      SC5P(11) = C5P(46) +C5P(47) +C5P(48)
      SLLHC(12)= LLHC(49)
      SC5P(12) = C5P(49)
      SLLHC(13)= LLHC(50)
      SC5P(13) = C5P(50)
      LAR=0
      DO I=4,13
      LAR=LAR+SLLHC(I)
      END DO
C
C***************LUMPED TOTAL HYDROCARBON DISTRIBUTION********************
C
      DO I=1,5
      LTHC(I) = THC(I)
      END DO
      LTHC(6) = THC(7)
      LTHC(7) = THC(9)
      LTHC(8) = THC(8) + THC(10) + THC(11)
      LTHC(9) = SC5P(1) + SC5P(3)
      LTHC(10) = SC5P(2)
      LTHC(11) = SC5P(4)+SC5P(5)+SC5P(6)+SC5P(7)+SC5P(8)
      LTHC(12) = SC5P(9)+SC5P(10)+SC5P(11)+SC5P(12)+SC5P(13)
      DO I=9,12
      LTHC(I) = LTHC(I)*(1-.01*THC4M)
      END DO
C
C******CALCULATION OF PARAFINS/AROMATICS RATIO************************
C
C     PARA = THC(3)/PM(3) + THC(5)/PM(5) + THC(7)/PM(7) + THC(9)/PM(9)
C    $      + THC(12)/PM(12) + THC(
C
C*******************PRINTING OF TABLES OF LUMPED DISTRIBUTIONS**********
C
      WRITE(NO,680)
  680 FORMAT(//////////,5X,5'*','LUMPED LIQUID & TOTAL C5+ HYDROCARBON
     $ MASS DISTRIBUTIONS',5'*',/)
      WRITE(NO,682)
  682 FORMAT(1X,'COMPOUND',31X,'LIQUID',14X,'TOTAL',//)
      DO I=1,50
      WRITE(NO,684) LHCNAME(I),LLHC(I),C5P(I)
      END DO
  684 FORMAT(1X,A30,7X,F6.2,13X,F6.2)
C
      WRITE(NO,690)
  690 FORMAT(////////////,3X,5'*','SUMMARY TABLE OF LIQUID & TOTAL C5+
     $ HYDROCARBON COMPOSITIONS',5'*',/)
      WRITE(NO,692)
  692 FORMAT(1X,'COMPOUND',38X,'LIQUID',14X,'TOTAL',//)
      DO I=1,13
      WRITE(NO,694) LLNAME(I),SLLHC(I),SC5P(I)
      END DO
  694 FORMAT(1X,A40,4X,F7.2,10X,F7.2)
C
      WRITE(NO,700)
  700 FORMAT(//,10X,5'*','LUMPED TOTAL HYDROCARBON MASS DISTRIBUTION',
     $5'*',/)
      WRITE(NO,702)
  702 FORMAT(1X,'COMPOUND',31X,'WEIGHT % OF TOTAL HYDROCARBONS',//)
      DO I=1,5
      WRITE(NO,710) NAME(I),LTHC(I)
      ENDDO
      DO I=6,8
      WRITE(NO,710) LNAME(I),LTHC(I)
      END DO
      WRITE(NO,704)
  704 FORMAT(/,1X,'C5+ HYDROCARBONS',/)
      DO I=9,12
      WRITE(NO,710) LNAME(I),LTHC(I)
      END DO
  710 FORMAT(1X,A40,12X,F7.2)
C
C************************************************************************
C                        UNLOCKING THE PRINTER
C************************************************************************
C     OPTION = 140000B
c     CALL LURQ (OPTION, LUARY, NUMLUS)
C
      STOP
      END
```

PROGRAM "PROFIL"

```
100 CLS
200 TR(10),TM(10),TW(10),TC(10),TR1(10),TM1(10),TW1(10),TRC(10),-
TMC(10).TWC(10),TCC(10),TRC1(10),TMC1(10),TWC1(10).TCC1(10),X-
(10),XC(10),TAV(10),TAVC(10)
300 PRINT "PROFILE DE TEMPERATURE INITIALE"
325 INPUT"DONNER LE NUMERO DE L'ESSAI";D$
350 INPUT"VOULEZ-VOUS REFAIRE DES CALCULS";A$
400 INPUT "DONNER LE NOM DU FICHIER INITIAL";N$
550 INPUT "DONNER LE NOM DU FICHIER FINAL";F$
560 INPUT "DONNER LE NOM DU FICHIER FINAL CORRIGE";F1$
600 CLS
650 IF A$="OUI" OR A$="oui" THEN 2110
700 FOR I=1 TO 10
800 PRINT "TC(";I;") =";:INPUT TC(I)
900 NEXT I
1000 CLS
1100 FOR I=1 TO 10
1200 PRINT "TM(";I;") =";:INPUT TM(I)
1300 NEXT I
1400 CLS
1500 FOR I=1 TO 10
1600 PRINT "TW(";I;") =";:INPUT TW(I)
1700 NEXT I
1800 CLS
1900 FOR I=1 TO 5
2000 PRINT "TR(";I;") =";:INPUT TR(I)
2100 NEXT I
2105 GOTO 2200
2110 OPEN N$ FOR INPUT AS #1
2120 FOR I=1 TO 10
2130 INPUT #1.TC(I),TM(I),TW(I),TR(I)
2140 NEXT I
2180 CLOSE #1
2200 FOR I=1 TO 10
2300 STC= STC + TC(I)+TM(I)+TW(I)+TR(I)
2600 NEXT I
3300 MTR=STC/35
3400 FOR I=1 TO 10
3500 T1(I)=TC(I)-MTR
3600 T2(I)=TM(I)-MTR
3700 T3(I)=TW(I)-MTR
3800 NEXT I
3900 FOR I=1 TO 5
4000 T4(I)=TR(I)-MTR
4100 NEXT I
4200 OPEN N$ FOR OUTPUT AS #1
4300 FOR I=1 TO 10
4400 PRINT #1.TC(I);",";TM(I);",":TW(I);",";TR(I)
4500 NEXT I
4900 CLOSE #1
5705 IF A$="OUI" OR A$="oui" GOTO 7310
5800 CLS:PRINT "PROFIL DE TEMPERATURE DE LA REACTION"
5900 FOR I=1 TO 10
6000 PRINT "TC1(";I;") =";:INPUT T5(I)
```

```
6100 NEXT I
6200 CLS
6300 FOR I=1 TO 10
6400 PRINT "TM1(";I;") =";:INPUT T6(I)
6500 NEXT I
6600 CLS
6700 FOR I=1 TO 10
6800 PRINT "TW1(";I;") =";:INPUT T7(I)
6900 NEXT I
7000 CLS
7100 FOR I=1 TO 5
7200 PRINT "TR1(";I;") =";:INPUT T8(I)
7300 NEXT I
7305 GOTO 7400
7310 OPEN F$ FOR INPUT AS #1
7320 FOR I=1 TO 10
7330 INPUT #1.X(I).T5(I),T6(I).T7(I).XC(I),T8(I)
7340 NEXT I
7380 CLOSE #1
7400 FOR I=1 TO 10
7500 TA(I)=T5(I)-T1(I)
7600 TB(I)=T6(I)-T2(I)
7700 TF(I)=T7(I)-T3(I)
7800 NEXT I
7900 FOR I=1 TO 5
8000 TD(I)=T8(I)-T4(I)
8100 NEXT I
8110 FOR I=1 TO 10
8120 TE(I)=(7/26*T5(I))+(8/26*T6(I))+(11/26*T7(I))
8130 TG(I)=(7/26*TA(I))+(8/26*TB(I))+(11/26*TF(I))
8140 NEXT I
8150 FOR I=1 TO 5
8160 READ XC(I)
8170 NEXT I
8180 DATA 0.056,0.456,0.856,1.256,1.656
8181 FOR I=1 TO 10
8182 READ X(I)
8183 NEXT I
8184                                                          DATA
0.006,0.156,0.356,0.556,0.756,0.956,1.156,1.356,1.556,1.706
8200 OPEN F$ FOR OUTPUT AS #1
8300 FOR I=1 TO 10
8400                                                          PRINT
#1.X(I);",";T5(I);".";T6(I):",";T7(I):",";XC(I);",";T8(I)
8500 NEXT I
8900 CLOSE #1
9000 OPEN F1$ FOR OUTPUT AS #1
9100 FOR I=1 TO 10
9200  PRINT  #1,X(I);"  ";TA(I):"  ";TB(I);"  ";TF(I);" ";XC(I);"
":TD(I)
9300 NEXT I
9700 CLOSE #1
9750 CLS
9800 FOR I=1 TO 10
```

```
9850 LOCATE 4+I,20
9900 PRINT USING "###.##      ";X(I);TC(I);TM(I);TW(I);:PRINT
10000 NEXT I
10100 FOR I=1 TO 5
10150 LOCATE 16+I,20
10200 PRINT USING "###.##     ";XC(I);TR(I);:PRINT :NEXT I
10275 IF INKEY$="" THEN GOTO 10275
10280 CLS
10300 FOR I=1 TO 10
10350 LOCATE 4+I,20
10400 PRINT USING "###.##     ";X(I);T5(I);T6(I);T7(I);:PRINT
10410 NEXT I
10420 FOR I=1 TO 5
10425 LOCATE 16+I,20
10430 PRINT USING "###.##     ";XC(I);T8(I);:PRINT :NEXT I
10445 IF INKEY$="" THEN GOTO 10445
10447 CLS
10450 FOR I=1 TO 10
10475 LOCATE 4+I,20
10500 PRINT USING "###.##     ";X(I);TA(I);TB(I);TF(I);:PRINT
10510 NEXT I
10520 FOR I=1 TO 5
10525 LOCATE 16+I,20
10530 PRINT USING "###.##     ";XC(I);TD(I);:PRINT:NEXT I
10600 PRINT:PRINT "MEAN TEMPERATURE";MTR
10700 IF INKEY$="" THEN GOTO 10700
11000 CLS: PRINT"VOULEZ-VOUS IMPRIMER VOS RESULTATS"
12000    LPRINT"
******************************************"
12010 LPRINT"                  *
 *"
12020 LPRINT"                   *          TEMPERATURE PROFILE
 *"
12030 LPRINT"                  *             ESSAI : ";D$;"
     *"
12045 LPRINT"                   *
 *"
12050   LPRINT"
******************************************"
12060 LPRINT:LPRINT:LPRINT
12100 LPRINT"                TEMPERATURE READINGS BEFORE REACTANTS
FEEDING"
12105    LPRINT"
-----------------------------------------------":LPRINT
12110 LPRINT"                            ** REACTOR SIDE **"
12130 LPRINT:LPRINT"                        x (m)    TC (C)       TH
(C)      TW (C)":LPRINT
12135 FORMAT1$="       ###.#"
12136 FORMAT2$="          ###.#"
12137 FORMAT3$="    #.###"
12140 FOR I=1 TO 10
12145 IF I=10 THEN FORMAT3$="      #.###"
12150 LPRINT "      LEVEL     ";I;:LPRINT USING FORMAT3$;X(I);:LPRINT
USING  FORMAT1$;TC(I);:LPRINT  USING FORMAT1$;TM(I);:LPRINT USING
```

```
FORMAT1$;TW(I)
12160 NEXT I
13060 LPRINT:LPRINT
13110 LPRINT"                                    ** COOLANT SIDE **"
13130 LPRINT:LPRINT"                             x (m)      TC (C)":LPRINT
13135 FORMAT3$="     #.###"
13140 FOR I=1 TO 5
13150 LPRINT "    LEVEL  ";I;:LPRINT USING FORMAT3$;XC(I);:LPRINT
USING FORMAT1$;TR(I)
13160 NEXT I
14060  LPRINT:LPRINT  "       INITIAL MEAN TEMPERATURE: ";:LPRINT
USING "###.##";MTR
14100 LPRINT:LPRINT:LPRINT"                        TEMPERATURE READINGS
DURING THE REACTION"
14105    LPRINT"
----------------------------------------":LPRINT
14110 LPRINT"                                    ** REACTOR SIDE **"
14130 LPRINT:LPRINT"                             x (m)      TC (C)       TH
(C)      TW (C)     TAV (C)":LPRINT
14135 FORMAT3$="     #.###"
14140 FOR I=1 TO 10
14145 IF I=10 THEN FORMAT3$="    #.###"
14150 LPRINT  "    LEVEL  ";I;:LPRINT USING FORMAT3$;X(I);:LPRINT
USING FORMAT1$;T5(I);:LPRINT  USING  FORMAT1$;T6(I);:LPRINT USING
FORMAT1$;T7(I);:LPRINT USING FORMAT1$;TE(I)
14160 NEXT I
14200
LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT:LPRINT
14270 LPRINT"                                    ** COOLANT SIDE **"
14280 LPRINT
14290 LPRINT"                     x (m)      TC (C)":LPRINT
14295 FORMAT3$="     #.###"
14300 FOR I=1 TO 5
14350 LPRINT "    LEVEL  ";I;:LPRINT USING FORMAT3$;XC(I);:LPRINT
USING FORMAT1$;T8(I)
14360 NEXT I
15000 LPRINT: LPRINT:LPRINT:LPRINT
15003 LPRINT"                  REVISED  TEMPERATURE PROFILE  FOR THE
REACTION"
15004    LPRINT"
-------------------------------------------":LPRINT
15006 LPRINT"                                   ** REACTOR SIDE **"
15009 LPRINT
15015 LPRINT"                     x (m)      TC (C)      TH  (C)
TW (C)      TAV (C)":LPRINT
15017 FORMAT3$="     #.###"
15020 FOR I=1 TO 10
15025 IF I=10 THEN FORMAT3$="    #.###"
15030 LPRINT  "    LEVEL  ";I;:LPRINT USING FORMAT3$;X(I);:LPRINT
USING FORMAT1$;TA(I);:LPRINT  USING  FORMAT1$;TB(I);:LPRINT USING
FORMAT1$;TF(I);:LPRINT USING FORMAT1$;TG(I)
15040 NEXT I
15060 LPRINT:LPRINT
15110 LPRINT"                                   ** COOLANT SIDE **"
```

```
15120 LPRINT
15130 LPRINT"                        x (m)     TC (C)":LPRINT
15137 FORMAT3$="     #.###"
15140 FOR I=1 TO 5
15150 LPRINT "    LEVEL  ";I;:LPRINT USING FORMAT3$;XC(I);:LPRINT
USING FORMAT1$;TD(I)
15160 NEXT I
15200 LPRINT: LPRINT
^Z
```

```
ftn7x,1,s
$cds on
$files 0,2

      Program enthalpy4
c
c******************************************
c         Enthalpies calculation
c******************************************
c
          character*10 num,srn*15
          character*18 datafile1,datafile2
          real lndt
c
c******************************************
c               Input data
c******************************************
c
      write (1,*) 'File designation'
      read (1,*) num
      write (1,*) 'Temperature gas in'
      read (1,*) tgin
      write (1,*) 'Temperature gas out'
      read (1,*) tgout
      write (1,*) 'Temperature coolant in'
      read (1,*) tcin
      write (1,*) 'Temperature coolant out'
      read (1,*) tcout
      write (1,*) 'CO conversion'
      read (1,*) coconv
c
c******************************************
c
      iend = index(num,' ')
      srn=num(1:iend-1) // '.dat'
      datafile1 = 'poe' // srn
      datafile2 = 'pom' // srn
      open (10,file = datafile1)
      read (10,*) wCH4,wC2,wC3,wC4,wC5,wC6,wbe,wto,wxy,wtri,wtmb
      close(10)
      open (20,file = datafile2)
      read (20,*) tg,frinco,frinh2,frout,wc,x1,x2,x3,pCO,pH2,pM,pHC,
     $            pH2O,pCO2
c
c*******************************
c         CALCULATIONS
c*******************************
c
      tgin=tgin+273
      tgout=tgout+273
      tcin=tcin+273
      tcout=tcout+273
c ***** molar fraction of HC *****
      xt=wCH4/16+wC2/28+wC3/44+wC4/58+wC5/72+wC6/86+wbe/78+wto/92
     $   +wxy/106+wtri/120+wtmb/134
```

```
      xCH4=wCH4/16/xt
      xC2=wC2/28/xt
      xC3=wC3/44/xt
      xC4=wC4/58/xt
      xC5=wC5/72/xt
      xC6=wC6/86/xt
      xbe=wbe/78/xt
      xto=wto/92/xt
      xxy=wxy/106/xt
      xtri=wtri/120/xt
      xtmb=wtmb/134/xt
      wm=xCH4*16+xC2*28+xC3*44+xC4*58+xC5*72+xC6*86+xbe*78
     $   +xto*92+xxy*106+xtri*120+xtmb*134
c ***** cp gas in *****
      frint=frinco+frinh2
      t=tgin
      cpCO=(30.87-1.285e-2*t+2.789e-5*t**2-1.272e-8*t**3)
      cpH2=(6.62+0.00081*t)/.239
      cpgasin=((frinh2/frint*cph2)+(frinco/frint*cpco))*.239
      wtin=(frinco/frint*28)+(frinh2/frint*2)
      cpgasin=cpgasin/wtin
c ***** cp gas out *****
      t = tgout
      cpCO=(30.87-1.285e-2*t+2.789e-5*t**2-1.272e-8*t**3)
      cpH2=(6.62+0.00081*t)/.239
      cpM=(21.15+7.092e-2*t+2.587e-5*t**2-2.852e-8*t**3)
      cpCH4=(19.25+5.213e-2*t+1.197e-5*t**2-1.132e-8*t**3)
      cpC2=(5.409+1.781e-1*t-6.938e-5*t**2+8.713e-9*t**3)
      cpC3=(-4.224+3.063e-1*t-1.586e-4*t**2+3.215e-8*t**3)
      cpC4=(9.487+3.313e-1*t-1.108e-4*t**2-2.822e-9*t**3)
      cpC5=(-3.626+4.873e-1*t-2.58e-4*t**2+5.305e-8*t**3)
      cpC6=(-4.413+5.82e-1*t-3.119e-4*t**2+6.494e-8*t**3)
      cpbe=(-33.92+4.739e-1*t-3.017e-4*t**2+7.13e-8*t**3)
      cpto=(-24.35+5.125e-1*t-2.765e-4*t**2+4.911e-8*t**3)
      cpxy=(-29.17+6.297e-1*t-3.747e-4*t**2+8.478e-8*t**3)
      cptri=(-4.668+6.238e-1*t-3.263e-4*t**2+6.376e-8*t**3)
      cptmb=(3.923+7.131e-1*t-3.711e-4*t**2+6.84e-8*t**3)
      cpHC=(xCH4*cpCH4+xC2*cpC2+xC3*cpC3+xC4*cpC4+xC5*cpC5+xC6*cpC6+
     $     xbe*cpbe+xto*cpto+xxy*cpxy+xtri*cptri+xtmb*cptmb)
      cpH2O=(32.24+1.924e-3*t+1.055e-5*t**2-3.596e-9*t**3)
      cpCO2=(19.8+7.344e-2*t-5.602e-5*t**2+1.715e-8*t**3)
      cpgasout=(pCO*cpCO+pH2*cpH2+pM*cpM+pHC*cpHC+pH2O*cpH2O+pCO2*cpCO2)
     $*.239
      wt=(pCO*18+pH2*2+pM*32+pHC*wm+pH2O*18+pCO2*44)
      cpgasout=cpgasout/wt
c ***** cp gas mean *****
      cpgas=(cpgasin+cpgasout)/2
c ***** cp coolant in *****
      t=tcin
      cpcin=0.00035*t+0.348
c ***** cp coolant out *****
      cpcout=0.00035*tcout+0.348
c ***** cp coolant mean *****
      cpc=(cpcin+cpcout)/2
c ***** enthalpy calculation *****
```

```
      enth1=-23983.4
      enth3=-9217.0
      flow=frint*60/24.2/1000*wtin
      dtg=(tgout-tgin)
      dtc=(tcout-tcin)
      dtin=tgin-tcin
c     if (dtin.eq.0) goto 200
c     lndt=((tgin-tcin)-(tgout-tcout))/(log((tgin-tcin)/(tgout-tcout)))
c     goto 250
c 200 lndt=(tgout-tcout)/2
  250 enthgas=flow*cpgas*(tgout-tgin)
      enthc=wc*cpc*(tcout-tcin)
      enthrt=-(enthgas+enthc)
      flowco=(frinco*60/24.2/1000)*coconv/100
      enthgl=enthrt/flowco
      enth13=x1*enth1
      enth132=x3*enth3
      enth2=(enthrt-enth13-enth132)/x2
c     ua=enthc/lndt
c
c*************************************************
c                  OUTPUT
c*************************************************
c
      write (1,10) enthrt
   10 format (7x,'enthrt= ',f8.1)
      write (1,20) enth13
   20 format (7x,'enth13 = ',f8.1)
      write (1,30) enth132
   30 format (7x,'enth132 = ',f8.1)
      write (1,40) enthgl
   40 format (7x,'enthgl =',f8.1)
      write (1,50) enth2,dtc
   50 format (7x,'enth2=',f8.1,/,7x,'dt coolant=',f4.1)
      write (1,60) lndt,ua
   60 format (7x,'lndt= ',f4.1,/,7x,'ua= ',f8.3)
      stop
      end
```

```
ftn7x,1,s

      Program OPTI

c*******************************************************************
c     Simulation program OPTI
c     1) Marquardt optimization of b and U.
c     2) Pseudohomogeneous one-dimensional model for
c        pseudoadiabatic tubular catalytic reactors
c        and the following reactions:
c
c        (1)  CO + 2 H2 --> CH3OH
c        (2)  CH3OH --> HC + H2O
c        (3)  CO + H2O <--> CO2 + H2
c
c        Solve using Fourth-order Runge-Kunta
c        method.
c*******************************************************************
c
c************************************
c     NOTATION - VARIABLES - UNITS
c************************************
c
c      a   group of parameters=(3.14159*r**2)*catd (kgcat/m)
c      aa  kinetic constant methanol synthesis reaction(kgcat*h*atm**3)/
c      ak1 parameter used Runge-Kutta method(kmol/(h*m))
c      ak2 parameter used Runge-Kutta method(Kmol/(h*m))
c      ak3 parameter used Runge-kutta method(Kmol/(h*m)
c      ak4 parameter used Runge-Kutta method(K/m)
c      aw  heat transfer coefficient near the wall(Kcal/(h*m**2*K))
c      a2  kinetic parameter=E/R (K)
c      bb  kinetic constant methanol synthesis(Kgcat*h*atm**4/Kmol)**1/3
c      biot Biot dimensionless number= aw*r/ker
c      b1 group of parameters involved in the heat balance(Kgcat*h*Kcal)/
c         (Kmol*m)
c      b11group of parameters involved in the heat balance(Kgcat*h*Kcal)/
c         (Kmol*m)
c      b111group of parameters involved in the heat balance
c      b2 natural logaritm of the preexponential factor
c      c  group pf parameters involved in the heat balance(1/m)
c      catd bulk density of the fixed bed(Kgcat/m**3)
c      cc kinetic constant for the methanol synthesis((Kgcat*h*atm**4)
c         /Kmol)**1/3
c      cpc heat capacity of the coolant(Kcal/Kg*K)
c      cpgas heat of the gas mixture(Kcal/Kg*K)
c      d   group of parameter(1/m)
c      dd  kinetic constant for the methanol synthesis((Kgcat*h*atm**4)/
c      de  equivalent diamter,square pitch arrengement(1/m)
c      der radial effective diffusivity(m**2/h)
c      dz  integration step(m)
c      d1  external tube diameter(m)
c      e   group of parameters(K/m)*(Kcat*h)/Kmol
c      enthl=enthalpy change synthesis of methanol(Kcal/Kmol CO consumed)
c      gasd=density ofthe gas mixture(Kg/m**3)
c      g = coolant flux(Kg/m**2*h)
```

```
c     gam1=weight fraction of active catalyst for methanol synthesis
c     gam2=weight fraction of active catalyst for methanol conversion
c     gg= gas mixture flux(Kg/m**2*h)
c     hid= coolant fluid density(Kg/m**3)
c     hout= shell side heat transfer coefficient(Kcal/m**2*h*K)
c     k =counter
c     kc=thermal conductivity of the collant(Kcal/(h*m*K))
c     ker=effective radial thermal conductivity of the bed(Kcal/(h*m*K))
c     kg=thermal conductivity of the gas mixture(Kcal)/(h*m*K)
c     keq=equilibrium constant(1/atm**2)
c     nCO0=molar flow of CO fed to the reactor(Kmol/h)
c     nH20=molar flow of H2 fed to the reactor(Kmol/h)
c     nt0=molar flow of reactants fed to the reactor(Kmol/h)
c     pemr=Peclet number= v*dp/der
c     prg=Prandtl number for the gas= cpgas*ug/kg
c     pt=total pressure in the reactor(atm)
c     pCO=partial pressure of CO(atm)
c     pH2=partial pressure of H2(atm)
c     pM=partial pressure of methanol(atm)
c     pHC=partial pressure of hydrocarbons(atm)
c     pH2O=partial pressure of H2O(atm)
c     pCO2=partial pressure of CO2(atm)
c     r = internal tube radius(m)
c     rCO= rate of methanol formation (Kmol/h/kgcat)
c     rH2O= rate of methanol conversion (Kmol/h/kgcat)
c     reg=Reynolds number for the gas=dp*gg/ug
c     t =bed temperature(K)
c     tc=coolant temperature(K)
c     tn=total number of tubes
c     u=overall heat transfer coefficient(Kcal/m**2*h*K)
c     uc=viscosity of the coolant(kg/m*h)
c     ug=viscosity of the gas mixture(kg/m*h)
c     v=superficial gas velocity(m/h)
c     wc=coolant flow(Kg/s)
c     wt=molecular weight of the gas mixture(Kg/Kmol)
c     x1=progress of the methanol synthesis reaction(Kmol/h)
c     x2=progress of the methanol conversion reaction(Kmol/h)
c     x3=progress of the wgs reaction(Kmol/h)
c
c************************************************************
c          Marquardt Optimization of b and U
c
c     NOTE: Notation listed in appendix
c
c************************************************************

      DIMENSION A(10,10),AC(10,10),BMIN(10),BMAX(10)
      real P(50)
      real Z(25), Y(25), BY(16),BV(10),B(10), ty(16)
      character Rn*10
      character*10 Datafile*16,datafile2*16,Rns,Rname
      EXTERNAL FUNC
      external runge
      common x
c
```

```
      call fparm( Rn )
c
     ✓NN=16
     ✓KK=2
c
c     write(1,*) 'ENTER # OF THE RUN'
c     read(1,'(a6)') Rn
      iend = index(Rn,' ')
      Rns = Rn(1:iend-1) // '.DAT'
      Datafile = 'OPT' // Rns
      Datafile2= 'res' // Rns
      open (10,FILE=datafile)
      read (10,*) (by(i), i=1,16)
      close(10)
      do i=1,15
      y(i)=by(i)
      end do
      y(16)=by(16)
      b(1)=7.
      b(2)=100.
      bmin(1)=1.
      bmax(1)=15.
      bmin(2)=30.
      bmax(2)=500.
C
      FNU = 0.0
      FLA = 0.0
      TAU = 0.0
      EPS = 0.0
      PHMIN = 0.0
      I = 0
      KD = KK
      FV = 0.0
      DO J = 1, KK
          BV(J) = 1
      END DO
      ICON = KK
      ITER = 0
      NO = 1
      WRITE (NO,15)
15    FORMAT ( 10X,27HBSOLVE REGRESSION ALGORITHM)
C
200   CALL BSOLVE(KK,B,NN,Z,Y,PH,FNU,FLA,TAU,EPS,PHMIN,I,ICON,FV,DV,BV,
     $BMIN,BMAX,P,FUNC,DERIV,KD,A,AC,GAMM,runge,rn,ty)
C
      ITER = ITER + 1
      WRITE (NO,1) ICON, PH, ITER
1     FORMAT (9X,6HICON = , I3, 4X, 5HPH = , E15.8, 4X,
     $16HIteration No. = , I3)
      IF (ICON) 10, 300, 200
10    IF (ICON+1) 20, 60, 200
20    IF (ICON+2) 30, 70, 200
30    IF (ICON+3) 40, 80, 200
40    IF (ICON+4) 50, 90, 200
50    GO TO 95
```

```
60    WRITE (NO,4)
4     FORMAT (//, 9X, 32HNo Function Improvement Possible )
      GO TO 300
70    WRITE (NO,5)
5     FORMAT (//,9X, 28HMore Unknowns than Functions)
      GO TO 300
80    WRITE (NO, 6)
6     FORMAT (//,9X, 2HTotal Variables are Zero)
      GO TO 300
90    WRITE (NO,7)
7     FORMAT (//,9X,79HCorrections Satisfy Convergence Requirements but
     $Lamda Factor (FLA) still Large)
      GO TO 300
95    WRITE (NO,8)
8     FORMAT (//,9X, 20HThis is not Possible)
      GO TO 300
300   OPEN (10, FILE=DATAFILE2)
      WRITE (10,*) RN
      WRITE (10,*) B(1),B(2),PH
      WRITE (10,*) (bY(I), I=1,16)
      WRITE (10,*) (ty(I), I=1,16)
      CLOSE(10)
1000  STOP
      END
c
c***********************************************************
      SUBROUTINE FUNC ( KK, B, NN, Z, FV , runge, rn, ty)
c
c     NOTE: Notation at the beginning of the program.
c***********************************************************
c
c******************************
c     VARIABLE DEFINITIONS
c******************************
c
      real kc,kg,hid,ker,keq,nt,nt0,nCO0,nH20,kCO,kH2,kHC,kM,kH20
      real k,mcat,kCO2,kwgs
      integer N
      character*10 rn,srn*15
      character*18 datafile
      real vct(1000),vctc(1000),vz(1000),b(20),z(25),ty(20)
      iend = index(rn,' ')
      srn = rn(1:iend-1) // '.dat'
      datafile = 'poc' // srn
      open (10,file = datafile)
      read (10,*) pt,flow,beta,wc,td,tsc,t,tc,enth1
      close (10)
      tgi=t
      corr1=b(1)
      corr2=b(2)
      write(1,3000) corr1,corr2
3000  format(7x,'b=',f8.4,2x,'U=',f6.1)
c
c**************************
c     INITIAL VALUES
```

```
c***************************
c
  630 gam1=0.63
      gam2=0.27
      a2=10555
      b2=15.48
      dz=0.004
      t=t+273.
      tc=tc+273.
      ct=t-273.
      ctc=tc-273.
      wc=wc/3600
      cwc=wc*3600
      catd=795.0
      r=0.0105
      tn=1
      d1=0.0266
      d2=0.0351
      x1=0.
      x2=0.
      x3=0.
      mcat=.55
      nt0=flow*60/24.2/1000
      nt=nt0
      nCO0=nt0/(1+beta)
      nH20=beta*nCO0
      wt=(28*nCO0+2*nH20)/(nCO0+nH20)
      pCO=nCO0/nt0*pt
      pH2=nH20/nt0*pt
      pM=0.
      pHC=0.
      pH2O=0.
      pCO2=0.
      de=(d2**2-d1**2)/4/d1
      zz=0.0
      zt=1.856
      dmcat=mcat*(dz/zt)
      ak1=0
      ak2=0
      ak3=0
      ak4=0
      nnn=0
      k=0
c
c********************************************
c             CALCULATIONS (1)
c********************************************
c
      iend = index(rn,' ')
      srn=rn(1:iend-1) // '.dat'
      datafile = 'poe' // srn
      open (10,file = datafile)
      read (10,*) wCH4,wC2,wC3,wC4,wC5,wC6,wbe,wto,wxy,wtri,wtmb
      close(10)
      xt=wCH4/16+wC2/28+wC3/44+wC4/58+wC5/72+wC6/86+wbe/78+wto/92
```

```
     $   +wxy/106+wtri/120+wtmb/134
      xCH4=wCH4/16/xt
      xC2=wC2/28/xt
      xC3=wC3/44/xt
      xC4=wC4/58/xt
      xC5=wC5/72/xt
      xC6=wC6/86/xt
      xbe=wbe/78/xt
      xto=wto/92/xt
      xxy=wxy/106/xt
      xtri=wtri/120/xt
      xtmb=wtmb/134/xt
c***** Molecular weight of hydrocarbons *****
      wm=xCH4*16+xC2*28+xC3*44+xC4*58+xC5*72+xC6*86+xbe*78+
     $   xto*92+xxy*106+xtri*120+xtmb*134
c***** Average carbon number of hydrocarbons *****
      nc=xCH4*1+xC2*2+xC3*3+xC4*4+xC5*6+xC6*6+xbe*6+xto*7
     $   +xxy*8+xtri*9+xtmb*10
c***** Pourcentage of gasoline *****
      wgaso=(wC5+wC6+wbe+wto+wxy+wtri+wtmb)/100
c*********************************
c         CALCULATIONS (2)
c*********************************
c
  200 kkk=kkk+1
      alfa=1-(2*x1-(x2/nc))/nt0
      nt=nt0-2*x1+x2/nc
      gasd=(pt/0.08208/t)*wt
      v=nt/(3.14159*r**2*pt)*0.08208*t
C ------- cpgas -------
      cpCO=(30.87-1.285e-2*t+2.789e-5*t**2-1.272e-8*t**3)
      cpH2=(6.62+0.00081*t)/.239
      cpM=(21.15+7.092e-2*t+2.587e-5*t**2-2.852e-8*t**3)
      cpCH4=(19.25+5.213e-2*t+1.197e-5*t**2-1.132e-8*t**3)
      cpC2=(5.409+1.781e-1*t-6.938e-5*t**2+8.713e-9*t**3)
      cpC3=(-4.224+3.063e-1*t-1.586e-4*t**2+3.215e-8*t**3)
      cpC4=(9.487+3.313e-1*t-1.108e-4*t**2-2.822e-9*t**3)
      cpC5=(-3.626+4.873e-1*t-2.58e-4*t**2+5.305e-8*t**3)
      cpC6=(-4.413+5.82e-1*t-3.119e-4*t**2+6.494e-8*t**3)
      cpbe=(-33.92+4.739e-1*t-3.017e-4*t**2+7.13e-8*t**3)
      cpto=(-24.35+5.125e-1*t-2.765e-4*t**2+4.911e-8*t**3)
      cpxy=(-29.17+6.297e-1*t-3.747e-4*t**2+8.478e-8*t**3)
      cptri=(-4.668+6.238e-1*t-3.263e-4*t**2+6.376e-8*t**3)
      cptmb=(3.923+7.131e-1*t-3.711e-4*t**2+6.84e-8*t**3)
      cpHC=(xCH4*cpCH4+xC2*cpC2+xC3*cpC3+xC4*cpC4+xC5*cpC5+xC6*cpC6+
     $      xbe*cpbe+xto*cpto+xxy*cpxy+xtri*cptri+xtmb*cptmb)
      cpH2O=(32.24+1.924e-3*t+1.055e-5*t**2-3.596e-9*t**3)
      cpCO2=(19.8+7.344e-2*t-5.602e-5*t**2+1.715e-8*t**3)
      cpgas=(pCO*cpCO+pH2*cpH2+pM*cpM+pHC*cpHC+pH2O*cpH2O+pCO2*cpCO2)
     $/pt*.239
      wt=(pCO*28+pH2*2+pM*32+pHC*wm+pH2O*18+pCO2*44)/pt
      cpgas=cpgas/wt
c -------- viscosity gas ----------
      uCO=0.1105
      uH2=0.0533
      uM=0.0756
      uHC=0.054
      uH2O=0.081
      uCO2=0.1019
      ug=(pCO*uCO*28**0.5+pH2*uH2*2**0.5+pM*uM*32**0.5+pHC*uHC*wm**
     $0.5+pH2O*uH2O*18**0.5+pCO2*uCO2*44**0.5)/(pCO*28**0.5+pH2*2**0.5+
     $pM*32**0.5+pHC*wm**0.5+pH2O*18**0.5+pCO2*44**0.5)
c -------- thermal conductivity gas --------
      kCO=uCO*(cpCO+2.48/28.)
      kH2=uH2*(cpH2+2.48/2.)
      kM=uM*(cpM+2.48/32)
      kHC=uHC*(cpHC+2.48/wm)
      kH2O=uH2O*(cpH2O+2.48/18)
      kCO2=uCO2*(cpCO2+2.48/44)
      kg=(pCO*kCO*28**.33+pH2*kH2*2**.33+pM*kM*32**.33+pHC*kHC*wm**
     $.33+pH2O*kH2O*18**.33+pCO2*kCO2*44**.33)/(pCO*28**.33+pH2*2**.33+
     $pM*32**.33+pHC*wm**.33+pH2O*18**.33+pCO2*44**.33)
      kc=-0.00005*tc+0.1267
      hid=-0.4125*tc+1141.5
      uc=-0.0026*tc+3.137
      cpc=0.00035*tc+0.348
      g=(3600.0*wc)/(3.14159/4.*(d2**2-d1**2))
      u=corr2
      a=(3.14158*r**2)*catd
      b1=(-enth1*catd*gam1)/(v*cpgas*gasd)/alfa
      c=(2.0*u)/(v*cpgas*gasd*r)/alfa
      d=(2.0*3.14159*r*tn*u)/(wc*3600.0*cpc)
      e=(catd*t*wt )/(v*gasd*alfa)
c
c*****************************************
c    DIFFERENTIAL EQUATIONS RESOLUTION
c*****************************************
c
  300 zz=zz+dz
  301 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak10,ak20,ak30,ak40,x1,
     $x2,x3,t,tc,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,gam2,
     $dfac,nc,tsc,dx3,corr1)
      x11=x1+ak10/2.0*dz
      x21=x2+ak20/2.0*dz
      t1=t+ak30/2.0*dz
      tc1=tc+ak40/2.0*dz
  302 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak11,ak21,ak31,ak41,x11,
     $x21,x31,t1,tc1,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
      x12=x1+ak11/2.0*dz
      x22=x2+ak21/2.0*dz
      t2=t+ak31/2.0*dz
      tc2=tc+ak41/2.0*dz
  303 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak12,ak22,ak32,ak42,x12,
     $x22,x32,t2,tc2,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
      x13=x1+ak12*dz
      x23=x2+ak22*dz
      t3=t+ak32*dz
      tc3=tc+ak42*dz
  304 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak13,ak23,ak33,ak43,x13,
     $x23,x33,t3,tc3,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
      dx1=(dz/6.)*(ak10+(ak11*2.0)+(ak12*2.0)+ak13)
      x1=x1+dx1
      dx2=(dz/6)*(ak20+(ak21*2.0)+(ak22*2.0)+ak23)
      x2=x2+dx2
      dt=(dz/6)*(ak30+(ak31*2.0)+(ak32*2.0)+ak33)
      t=t+dt
      dtc=(dz/6)*(ak40+(ak41*2.0)+(ak42*2.0)+ak43)
      tc=tc+dtc
      tctr=t+(t-tc)*0.25*biot/(1+0.25*biot)
c ----- water-gas-shift reaction -------
      x31=x3
      nt1=nt
      dx3=0.
      ni=0.
      w=0.
      dw=0.
 320  w = w + dw
      kwgs = exp(3.296-(9170./1.987*(t-600.)/(600.*t)))
      af = (kwgs*(pH2O-w)*(pCO-w))-((pCO2+w)*(pH2+w))
      dfdw = -((kwgs*(pH2O-w))+(kwgs*(pCO-w))+(pCO2+w)+(pH2+w))
      dw = -af/dfdw
      ni=ni+1
      if (af.gt.0.001) goto 320
      pCO2=pCO2+w
      pH2=pH2+w
      pCO=pCO-w
      pH2O=pH2O-w
      nt=nt0-2*x1+x2/nc
      x3 = pCO2*nt/pt
      dx3= (x3-x31)
      ct=t-273
      ctc=tc-273
      ctctr=tctr-273
      nnn=nnn+1
      vct(nnn)=ct
      vctc(nnn)=ctc
      vz(nnn)=zz
      if (ct.gt.700) goto 325
c     write(1,*) 'Attention, tc is greater than 600 C!!'
      if (zz.lt.zt) goto 200
  325 nt=nt0-2*x1+x2/nc
      pflow=(nt*(1-(xgaso/xHC*pHC/pt))*24200/60)
      anCO=(pCO/pt)*nt
      conCO=(nCO0-anCO)/nCO0*100
      z(1)=tgi
      ty(1)=tgi
      do i=1,8
      z(i+1)=vct((39+(i-1)*50))
      ty(i+1)=z(i+1)
      end do
      z(10)=(vct(426)+vct(427))/2
      ty(10)=z(10)
      do i=1,5
      z(i+10)=vctc(14+(i-1)*100)
      ty(i+10)=vctc(14+(i-1)*100)
      end do
      z(16)=conco
      ty(16)=conco
      return
      end
c
c
c*****************************************************************
c     Subroutine runge contains the differential equations
c*****************************************************************
c
c
      subroutine runge (a,a1,a2,b1,b11,b111,b2,c d,e,ak1,ak2,ak3,ak4,x1,
     $x2,x3,t,tc,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,gam2,
     $dfac,nc,tsc,dx3,corr1)
      real keq,nCO0,nH20
      ak=1.5
      keq=exp(-(54.15-21660/t)/1.987)
      x1e=0.
      pM0=pM
  500 af=pt**2*(nCO0-x1e)*(nH20-2*x1e)**2*keq-x1e*(nCO0+nH20-2*x1e)**2
      dfdx1e=-(pt**2*(nH20-2*x1e)**2*keq+4*pt**2*(nCO0-x1e)*(nH20-2*
     $x1e)*keq+(nCO0+nH20-2*x1e)**2+4*x1e*(nCO0+nH20-2*x1e))
      dx1e=-af/dfdx1e
      x1e=x1e+dx1e
      pMeq=pt*x1e/(nCO0+nH20-2*x1e)
      dpMeq=abs(pMeq-pM0)
      if(dpMeq.lt.0.001) goto 510
      pM0=pMeq
      go to 500
  510 pCO=pt*(nCO0-x1-x3)/(nCO0+nH20-2*x1+x2/nc)
      pH2=pt*(nH20-2*x1+x3)/(nCO0+nH20-2*x1+x2/nc)
      pM=pt*(x1-x2)/(nCO0+nH20-2*x1+x2/nc)
      pHC=pt*x2/nc/(nCO0+nH20-2*x1+x2/nc)
      pH2O=pt*(x2-x3)/(nCO0+nH20-2*x1+x2/nc)
      pCO2=pt*x3/(nCO0+nH20-2*x1+x2/nc)
      t1=(1/t)-0.0015374
      aa=corr1*exp(-8340/1.789/t)
      bb=0.0329*exp(9682*t1/1.789)
      cc=0.0645*exp(8626*t1/1.789)
      ee=0.367*exp(1031*t1/1.789)
      rCO=((aa*pCO*pH2**2)/(1+bb*pCO+cc*pH2+ee*pCO2)**3)
     $*3600*1E-6
      rH2O=(pM*exp((-a2/t)+b2))/(1.0+ak*(pM+pH2O))
      dx1dz=a*rCO*gam1
      dx2dz=a*rH2O*gam2
      dtdz=(b1*rCO)-c*(t-tc)+e*(2*rCO*gam1-(rH2O*gam2/nc))
      dtcdz=d*(t-tc)
      ak1=dx1dz
      ak2=dx2dz
      ak3=dtdz
      ak4=dtcdz
      return
      end
C
C**********************************************************************
      SUBROUTINE BSOLVE ( KK, B, NN, Z, Y, PH, FNU, FLA, TAU, EPS,
     $ PHMIN, I, ICON, FV, DV, BV,  BM[N,BMAX,P, FUNC, DERIV, KD,
     $ A,AC,GAMM,runge,rn,ty)
C**********************************************************************
      DIMENSION A(10,10),AC(10,10),BMIN(10),BMAX(10)
      DIMENSION  Z(25), Y(25), BV(10),B(10), ty(20)
      DIMENSION P(50)
      character rn*6
C
      K = KK
      N= NN
      KP1 = K + 1
      KP2 = KP1 + 1
      KBI1 = K * N
      KBI2 = KBI1 + K
      KZI = KBI2 + K
      IF ( FNU .LE. 0. ) FNU = 10.0
      IF ( FLA .LE. 0. ) FLA = 0.01
      IF ( TAU .LE. 0. ) TAU = 0.001
      IF ( EPS .LE. 0. ) EPS = 0.00002
      IF ( PHMIN .LE. 0. ) PHMIN = 0.
120   KE = 0
130   DO 160 I1 = 1, K
160   IF ( BV(I1) .NE. 0. ) KE = KE + 1
      IF ( KE .GT. 0 ) GO TO 170
162   ICON = - 3
163   GO TO 2120
170   IF ( N .GE. KE ) GO TO 500
180   ICON = -2
190   GO TO 2120
500   I1 = 1
530   IF ( I .GT. 0 ) GO TO 1530
550   DO 560 J1 = 1, K
          J2 = KBI1 + J1
          P(J2) = B(J1)
          J3 = KBI2 + J1
560       P(J3) = ABS ( B(J1) ) + 1.0E-02
      GO TO 1030
590   IF ( PHMIN .GT. PH .AND. I .GT. 1 ) GO TO 625
      DO 620 J1 = 1, K
          N1 = ( J1 - 1 ) * N
          IF ( BV(J1) ) 601, 620, 605
601       CALL DERIV ( K, B, N, Z, P(N1+1), FV, DV, J1, JTEST )
          IF ( JTEST .NE. (-1) ) GO TO 620
          BV(J1) = 1.0
605       DO 606 J2 = 1, K
              J3 = KBI1 + J2
606       P(J3) = B(J2)
          J3 = KBI1 + J1
          J4 = KBI2 + J1
          DEN = 0.001 * AMAX1 ( P(J4), ABS(P(J3)))
          IF ( P(J3) + DEN .LE. BMAX(J1) ) GO TO 55
          P(J3) = P(J3) - DEN
          DEN = - DEN
          GO TO 56
55        P(J3) = P(J3) + DEN
56        CALL FUNC ( K, P(KBI1+1), N, P(N1+1), FV ,runge,rn,ty)
          DO 610 J2 = 1, N
               JB = J2 + N1
610            P(JB) = ( P(JB) - Z(J2) ) / DEN
620     CONTINUE
C
C       SET UP CORRECTION EQUATIONS
C
625     DO 725 J1 = 1, K
          N1 = ( J1 - 1 ) * N
          A(J1,KP1) = 0.
          IF ( BV(J1) ) 630, 692, 630
630       DO 640 J2 = 1, N
               N2 = N1 + J2
640            A(J1,KP1) = A(J1,KP1) + P(N2) * ( Y(J2) - Z(J2) )
650       DO 680 J2 = 1, K
660            A(J1,J2) = 0.
665            N2 = ( J2 - 1 ) * N
670            DO 680 J3 = 1, N
672                 N3 = N1 + J3
674                 N4 = N2 + J3
680       A(J1,J2) = A(J1,J2) + P(N3) * P(N4)
          IF (A(J1,J1).GT.1E-20) GO TO 725
          IF ( A(J1,J1) .GT. 1.E-20 ) GO TO 725
692       DO 694 J2 = 1, KP1
694            A(J1,J2) = 0.
695       A(J1,J1) = 1.0
725     CONTINUE
        GN = 0.
        DO 729 J1 = 1, K
729       GN = GN + A(J1,KP1) ** 2
C
C       SCALE CORRECTION EQUATIONS
C
        DO 726 J1 = 1, K
726       A(J1,KP2) = SQRT (A(J1,J1))
        DO 727 J1 = 1, K
          A(J1,KP1) = A(J1,KP1) / A(J1,KP2)
          DO 727 J2 = 1, K
727       A(J1,J2) = A(J1,J2)/ (A(J1,KP2)*A(J2,KP2))
730     FL = FLA / FNU
        GO TO 810
800     FL = FNU * FL
810     DO 840 J1 = 1, K
820       DO 830 J2 = 1, KP1
830            AC(J1,J2) = A(J1,J2)
840       AC(J1,J1) = AC(J1,J1) + FL
C
C       SOLVE CORRECTION EQUATIONS
C
```

```
      DO 930 L1 = 1, K
          L2 = L1 + 1
          DO 910 L3 = L2, KP1
910           AC(L1,L3) = AC(L1,L3) / AC (L1,L1)
          DO 930 L3 = 1,K
          IF (L1-L3) 920, 930, 920
920       DO 925 L4 = L2, KP1
925       AC(L3,L4) = AC(L3,L4) - AC(L1,L4) * AC(L3,L1)
930   CONTINUE
C
      DN = 0.
      DG = 0.
      DO 1028 J1 = 1, K
          AC(J1,KP2) = AC(J1,KP1) / A(J1,KP2)
          J2 = KBI1 + J1
          P(J2) = AMAX1 (BMIN(J1),AMIN1(BMAX(J1),B(J1)+AC(J1,KP2)))
          DG = DG + AC(J1,KP2) * A(J1,KP1) * A(J1,KP2)
          DN = DN + AC(J1,KP2) * AC(J1,KP2)
1028      AC(J1,KP2) = P(J2) - B(J1)
      COSG = DG / SQRT (DN*DG)
      JGAM = 0
      IF (COSG) 1100, 1110, 1110
1100  JGAM = 2
      COSG = - COSG
1110  CONTINUE
      COSG = AMIN1 (COSG, 1.0)
      GAMM = ARCOS(COSG) * 180. / (3.14159265)
      IF ( JGAM .GT. 0 ) GAMM = 180. - GAMM
1030  CALL FUNC (K, P(KBI1+1), N, P(KZI+1), FU,runge,rn,ty)
1500  PHI = 0.
C---------------------------------------
C     DO 1520 J1 = 1, N-1
C---------------------------------------
C***************************************
      DO 1520 J1 = 1, N-6
         J2 = KZI + J1
C***************************************
C---------------------------------------
C 1520      PHI = PHI + ((P(J2)-Y(J1))/(y(n-1)-y(1)))**2
C---------------------------------------
C***************************************
1520     PHI = PHI + ((P(J2)-Y(J1))/(Y(N-6)-Y(1)))**2
      DO 1522 J1= N-5, N-1
        J2 = KZI + J1
1522    PHI = PHI + ((P(J2)-Y(J1))/(Y(N-1)-Y(N-5)))**2
C***************************************
         j1 = j1 + 1
         j2 = kzi + j1
         phi = phi + ((p(j2)-y(j1))/y(n))**2
      IF (PHI .LT. 1.E-20 ) GO TO 3000
      IF ( I .GT. 0 ) GO TO 1540
1521  ICON = K
      GO TO 2110
1540  IF ( PHI .GE. PH ) GO TO 1530
C
```

```
C     EPSILON TEST
C
1200  ICON = 0
      DO 1220 J1 = 1, K
          J2 = KBI1 + J1
1220      IF(ABS(AC(J1,KP2))/(TAU+ABS(P(J2))) .GT. EPS) ICON = ICON + 1
      IF ( ICON .EQ. 0 ) GO TO 1400
C
C     GAMMA LAMBDA TEST
C
      IF ( FL .GT. 1.0 .AND. GAMM .GT. 90.0 ) ICON = - 1
      GO TO 2105
C
C     GAMMA EPSILON TEST
C
1400  IF ( FL .GT. 1.0 .AND. GAMM .LE. 45.0 ) ICON = - 4
      GO TO 2105
C
1530  IF ( I1 - 2 ) 1531, 1531, 2310
1531  I1 = I1 +1
      GO TO (530,590,800), I1
2310  IF ( FL .LT. 1.0E+8 ) GO TO 800
1320  ICON = - 1
C
2105  FLA = FL
      DO 2091 J2 = 1, K
          J3 = KBI1 + J2
2091      B(J2) = P(J3)
2110  DO 2050 J2 = 1, N
          J3 = KZI + J2
2050      Z(J2) = P(J3)
      PH = PHI
      I = I + 1
2120  RETURN
3000  ICON = 0
      GO TO 2105
C
      END
C
C     *******************************************************************
C
      FUNCTION ARCOS(Z)
C
      X = Z
      KEY = 0
      IF ( X .LT. (-1.) ) X= -1.
      IF ( X .GT. 1. ) X = 1.
      IF ( X .GE. (-1.) .AND. X .LT. 0. ) KEY = 1
      IF ( X .LT. 0. ) X = ABS (X)
      IF ( X .EQ. 0. ) GO TO 10
      ARCOS = ATAN (SQRT(1.-X*X) / X )
      IF ( KEY .EQ. 1 ) ARCOS = 3.14159265 - ARCOS
      GO TO 999
10    ARCOS = 1.5707963
999   RETURN
```

END

```
ftn7x,1,s

      Program simu

c*****************************************************************
c     Pseudohomogeneous one-dimensional model for
c     pseudoadiabatic tubular catalytic reactors
c     and the following reactions:
c
c     (1)  CO + 2 H2 --> CH3OH
c     (2)  CH3OH --> HC + H2O
c     (3)  CO + H2O <--> CO2 + H2
c*****************************************************************
c
c*********************************
c    NOTATION - VARIABLES - UNITS
c*********************************
c
c      a   group of parameters=(3.14159*r**2)*catd (kgcat/m)
c      aa  kinetic constant methanol synthesis reaction(kgcat*h*atm**3)/       c
c      ak1 parameter used Runge-Kutta method(kmol/(h*m))
c      ak2 parameter used Runge-Kutta method(Kmol/(h*m))
c      ak3 parameter used Runge-kutta method(Kmol/(h*m)
c      ak4 parameter used Runge-Kutta method(K/m)
c      aw  heat transfer coefficient near the wall(Kcal/(h*m**2*K))
c      a2  kinetic parameter=E/R (K)
c      bb  kinetic constant methanol synthesis(Kgcat*h*atm**4/Kmol)**1/3
c      biot Biot dimensionless number= aw*r/ker
c      b1 group of parameters involved in the heat balance(Kgcat*h*Kcal)/
c         (Kmol*m)
c      b11group of parameters involved in the heat balance(Kgcat*h*Kcal)/
c         (Kmol*m)
c      b111group of parameters involved in the heat balance
c      b2 natural logaritm of the preexponential factor
c      c  group pf parameters involved in the heat balance(1/m)
c      catd bulk density of the fixed bed(Kgcat/m**3)
c      cc kinetic constant for the methanol synthesis((Kgcat*h*atm**4)
c         /Kmol)**1/3
c      cpc heat capacity of the coolant(Kcal/Kg*K)
c      cpgas heat of the gas mixture(Kcal/Kg*K)
c      d   group of parameter(1/m)
c      dd  kinetic constant for the methanol synthesis((Kgcat*h*atm**4)/       c
c      de  equivalent diamter,square pitch arrengement(1/m)
c      der radial effective diffusivity(m**2/h)
c      dz  integration step(m)
c      d1  external tube diameter(m)
c      e   group of parameters(K/m)*(Kcat*h)/Kmol
c      enth1=enthalpy change synthesis of methanol(Kcal/Kmol CO consumed)
c      enth2=enthalpy change methanol conversion(Kcal/Kmol H2O formed)
c      enth3=enthalpy change wgs reaction(Kcal/Kmol CO2 formed)
c      gasd=density ofthe gas mixture(Kg/m**3)
c      g = coolant flux(Kg/m**2*h)
c      gam1=weight fraction of active catalyst for methanol synthesis
c      gam2=weight fraction of active catalyst for methanol conversion
c      gg= gas mixture flux(Kg/m**2*h)
```

```
c     hid= coolant fluid density(Kg/m**3)
c     hout= shell side heat transfer coefficient(Kcal/m**2*h*K)
c     k =counter
c     kc=thermal conductivity of the collant(Kcal/(h*m*K))
c     ker=effective radial thermal conductivity of the bed(Kcal/(h*m*K))
c     kg=thermal conductivity of the gas mixture(Kcal)/(h*m*K)
c     keq=equilibrium constant(1/atm**2)
c     nCO0=molar flow of CO fed to the reactor(Kmol/h)
c     nH20=molar flow of H2 fed to the reactor(Kmol/h)
c     nt0=molar flow of reactants fed to the reactor(Kmol/h)
c     pemr=Peclet number= v*dp/der
c     prg=Prandtl number for the gas= cpgas*ug/kg
c     pt=total pressure in the reactor(atm)
c     pCO=partial pressure of CO(atm)
c     pH2=partial pressure of H2(atm)
c     pM=partial pressure of methanol(atm)
c     pHC=partial pressure of hydrocarbons(atm)
c     pH2O=partial pressure of H2O(atm)
c     pCO2=partial pressure of CO2(atm)
c     r = internal tube radius(m)
c     rCO= rate of methanol formation (Kmol/h/kgcat)
c     rH2O= rate of methanol conversion (Kmol/h/kgcat)
c     reg=Reynolds number for the gas=dp*gg/ug
c     t =bed temperature(K)
c     tc=coolant temperature(K)
c     tn=total number of tubes
c     u=overall heat transfer coefficient(Kcal/m**2*h*K)
c     uc=viscosity of the coolant(kg/m*h)
c     ug=viscosity of the gas mixture(kg/m*h)
c     v=superficial gas velocity(m/h)
c     wc=coolant flow(Kg/s)
c     wt=molecular weight of the gas mixture(Kg/Kmol)
c     x1=progress of the methanol synthesis reaction(Kmol/h)
c     x2=progress of the methanol conversion reaction(Kmol/h)
c     x3=progress of the wgs reaction(Kmol/h)
c
c*****************************
c     VARIABLE DEFINITIONS
c*****************************
c
      real kc,kg,hid,ker,keq,nt,nt0,nCO0,nH20,kCO,kH2,kHC,kM,kH2O
      real k,mcat,kCO2,kwgs
      integer N
      character*10 num,srn*15
      character*18 datafile
      real vct(50),vctc(50),vctctr(50),vz(50),vpCO(50)
      real vpH2(50),vpM(50),vpHC(50),vpH2O(50)
      real vpCO2(50),vU(50),vx1(50),vx2(50),vx3(50)
      real va(50),vb1(50),vb11(50),vb111(50),vc(50)
      real vd(50),ve(50),vpMeq(50),vdt(50)
      real vcpc(50),vcpgas(50),vhout(50),vaw(50),vker(50)
c
c*****************************
c            INPUT
c*****************************
```

```
c
      write(1,*) ' U: '
      read(1,*) corr2
      write(1,*) ' b: '
      read(1,*) corr1
      write(1,*) 'Enter datafile designation:'
      read(1,'(A10)') num
      iend = index(num,' ')
      srn = num(1:iend-1) // '.dat'
      datafile = 'poc' // srn
      open (10,file = datafile)
      read (10,*) pt,flow,beta,wc,td,tsc,t,tc,enth1
      close (10)
c
c***********************************************
c     OUTPUT ADDRESS FOR RESULT PRINTING
c***********************************************
c
      write(1,*) 'Enter output address for result printing:'
      write(1,*) '    Screen: 1  ;  Printer: 6 '
      read(1,*) N
c
c*************************************************************
      write (N,30) num
   30 format(//,1x,20x,40'*',/,1x,20x,'*',38x,'*',/,
     $      1x,20x,'*',5x,'         SIMULATION         ',5x,'*',/,
     $      1x,20x,'*',38x,'*',/,
     $      1x,20x,'*',13x,'RUN PO',a8,11x,'*',/,1x,20x,'*',38x,'*',/,
     $      1x,20x,40'*',//)
c*************************************************************
c************************
c     INITIAL VALUES
c************************
c
  630 gam1=0.63
      gam2=0.27
      a2=10555
      b2=15.48
      dz=0.004
      t=t+273.
      tc=tc+273.
      ct=t-273.
      ctc=tc-273.
      wc=wc/3600
      cwc=wc*3600
      catd=795.0
      r=0.0105
      tn=1
      d1=0.0266
      d2=0.0351
      x1=0.
      x2=0.
      x3=0.
      mcat=.55
      nt0=flow*60/24.2/1000
      nt=nt0
      nCO0=nt0/(1+beta)
      nH20=beta*nCO0
      wt=(28*nCO0+2*nH20)/(nCO0+nH20)
      pCO=nCO0/nt0*pt
      pH2=nH20/nt0*pt
      pM=0.
      pHC=0.
      pH2O=0.
      pCO2=0.
      de=(d2**2-d1**2)/4/d1
      z=0.0
      zt=10.0
      dmcat=mcat*(dz/zt)
      ak1=0
      ak2=0
      ak3=0
      ak4=0
      nn=0
      k=0
c
c******************************************
c         Enthalpies calculation
c******************************************
c
      iend = index(num,' ')
      srn=num(1:iend-1) // '.dat'
      datafile = 'poe' // srn
      open (10,file = datafile)
      read (10,*) wCH4,wC2,wC3,wC4,wC5,wC6,wbe,wto,wxy,wtri,wtmb
      close(10)
      xt=wCH4/16+wC2/28+wC3/44+wC4/58+wC5/72+wC6/86+wbe/78+wto/92
     $   +wxy/106+wtri/120+wtmb/134
      xCH4=wCH4/16/xt
      xC2=wC2/28/xt
      xC3=wC3/44/xt
      xC4=wC4/58/xt
      xC5=wC5/72/xt
      xC6=wC6/86/xt
      xbe=wbe/78/xt
      xto=wto/92/xt
      xxy=wxy/106/xt
      xtri=wtri/120/xt
      xtmb=wtmb/134/xt
c***** Molecular weight of hydrocarbons *****
      wm=xCH4*16+xC2*28+xC3*44+xC4*58+xC5*72+xC6*86+xbe*78+
     $   xto*92+xxy*106+xtri*120+xtmb*134
c***** Average carbon number of hydrocarbons *****
      nc=xCH4*1+xC2*2+xC3*3+xC4*4+xC5*6+xC6*6+xbe*6+xto*7
     $   +xxy*8+xtri*9+xtmb*10
c***** Pourcentage of gasoline *****
      wgaso=(wC5+wC6+wbe+wto+wxy+wtri+wtmb)/100
c
c*****************************
c           OUTPUT
```

```
c******************************
c
      write(N,10)
   10 format(7x,30'*')
      write (N,12)
   12 format (11x,'SIMULATION CONDITIONS')
      write (N,14)
   14 format (7x,30'*',/)
      write (N,15) pt
   15 format (9x,'      Total pressure: ',f4.1,' atm')
      write (N,16) ct
   16 format (9x,'Reactant temperature: ',f5.1,' C')
      write (N,18) flow
   18 format (9x,'       Reactant flow: ',F5.2,' l/min')
      write (N,19) beta
   19 format (9x,'               H2/CO: ',F4.2)
      write (N,20) ctc
   20 format (9x,' Coolant temperature: ',f5.1,' C')
      write (N,22) cwc
   22 format (9x,'        Coolant flow: ',F4.1,' kg/hr')
      write (N,26) td
   26 format (9x,'       Test duration: ',I3,' min')
      write (N,23) tsc
   23 format (9x,'      Time on stream: ',F4.1,' hr',//)
c
c*********************************
c          CALCULATIONS
c*********************************
c
  200 kk=kk+1
      alfa=1-(2*x1-(x2/nc))/nt0
      nt=nt0-2*x1+x2/nc
      gasd=(pt/0.08208/t)*wt
      v=nt/(3.14159*r**2*pt)*0.08208*t
      cpCO=(30.87-1.285e-2*t+2.789e-5*t**2-1.272e-8*t**3)
      cpH2=(6.62+0.00081*t)/.239
      cpM=(21.15+7.092e-2*t+2.587e-5*t**2-2.852e-8*t**3)
      cpCH4=(19.25+5.213e-2*t+1.197e-5*t**2-1.132e-8*t**3)
      cpC2=(5.409+1.781e-1*t-6.938e-5*t**2+8.713e-9*t**3)
      cpC3=(-4.224+3.063e-1*t-1.586e-4*t**2+3.215e-8*t**3)
      cpC4=(9.487+3.313e-1*t-1.108e-4*t**2-2.822e-9*t**3)
      cpC5=(-3.626+4.873e-1*t-2.58e-4*t**2+5.305e-8*t**3)
      cpC6=(-4.413+5.82e-1*t-3.119e-4*t**2+6.494e-8*t**3)
      cpbe=(-33.92+4.739e-1*t-3.017e-4*t**2+7.13e-8*t**3)
      cpto=(-24.35+5.125e-1*t-2.765e-4*t**2+4.911e-8*t**3)
      cpxy=(-29.17+6.297e-1*t-3.747e-4*t**2+8.478e-8*t**3)
      cptri=(-4.668+6.238e-1*t-3.263e-4*t**2+6.376e-8*t**3)
      cptmb=(3.923+7.131e-1*t-3.711e-4*t**2+6.84e-8*t**3)
      cpHC=(xCH4*cpCH4+xC2*cpC2+xC3*cpC3+xC4*cpC4+xC5*cpC5+xC6*cpC6+
     $      xbe*cpbe+xto*cpto+xxy*cpxy+xtri*cptri+xtmb*cptmb)
      cpH2O=(32.24+1.924e-3*t+1.055e-5*t**2-3.596e-9*t**3)
      cpCO2=(19.8+7.344e-2*t-5.602e-5*t**2+1.715e-8*t**3)
      cpgas=(pCO*cpCO+pH2*cpH2+pM*cpM+pHC*cpHC+pH2O*cpH2O+pCO2*cpCO2)
     $/pt*.239
      wt=(pCO*28+pH2*2+pM*32+pHC*wm+pH2O*18+pCO2*44)/pt
      cpgas=cpgas/wt
      uCO=0.1105
      uH2=0.0533
      uM=0.0756
      uHC=0.054
      uH2O=0.081
      uCO2=0.1019
      ug=(pCO*uCO*28**0.5+pH2*uH2*2**0.5+pM*uM*32**0.5+pHC*uHC*wm**
     $0.5+pH2O*uH2O*18**0.5+pCO2*uCO2*44**0.5)/(pCO*28**0.5+pH2*2**0.5+
     $pM*32**0.5+pHC*wm**0.5+pH2O*18**0.5+pCO2*44**0.5)
      kCO=uCO*(cpCO+2.48/28.)
      kH2=uH2*(cpH2+2.48/2.)
      kM=uM*(cpM+2.48/32)
      kHC=uHC*(cpHC+2.48/wm)
      kH2O=uH2O*(cpH2O+2.48/18)
      kCO2=uCO2*(cpCO2+2.48/44)
      kg=(pCO*kCO*28**.33+pH2*kH2*2**.33+pM*kM*32**.33+pHC*kHC*wm**
     $.33+pH2O*kH2O*18**.33+pCO2*kCO2*44**.33)/(pCO*28**.33+pH2*2**.33+
     $pM*32**.33+pHC*wm**.33+pH2O*18**.33+pCO2*44**.33)
      kc=-0.00005*tc+0.1267
      uc=-0.0026*tc+3.137
      cpc=0.00035*tc+.348
      g=(3600*wc)/(3.141593/4.*(d2**2-d1**2))
      rec=0.0015*g/uc
      prc=cpc*uc/kc
      gg=v*gasd
      dp=0.0028
      reg=dp*gg/ug
      prg=cpgas*ug/kg
      write(1,*) reg,prg,rec,prc
      der=v*dp/(10.*(1.*19.4*(dp/(2.*r))**2.))
      pemr=v*dp/der
      ker=kg*(8.33+prg*reg/pemr)
      aw=kg/dp*exp(0.077+0.523*alog(reg))
      a=(3.14158*r**2)*catd
      b1=(-enth1*catd*gam1)/(v*cpgas*gasd)/alfa
      c=(2.0*u)/(v*cpgas*gasd*r)/alfa
      d=(2.0*3.14159*r*tn*u)/(wc*3600.0*cpc)
      e=(catd*t*wt )/(v*gasd*alfa)
c
c****************************************
c    DIFFERENTIAL EQUATIONS RESOLUTION
c****************************************
c
  300 z=z+dz
  301 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak10,ak20,ak30,ak40,x1,
     $x2,x3,t,tc,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,gam2,
     $dfac,nc,tsc,dx3,corr1)
      x11=x1+ak10/2.0*dz
      x21=x2+ak20/2.0*dz
      t1=t+ak30/2.0*dz
      tc1=tc+ak40/2.0*dz
  302 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak11,ak21,ak31,ak41,x11,
     $x21,x31,t1,tc1,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
```

```
      x12=x1+ak11/2.0*dz
      x22=x2+ak21/2.0*dz
      t2=t+ak31/2.0*dz
      tc2=tc+ak41/2.0*dz
  303 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak12,ak22,ak32,ak42,x12,
     $x22,x32,t2,tc2,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
      x13=x1+ak12*dz
      x23=x2+ak22*dz
      t3=t+ak32*dz
      tc3=tc+ak42*dz
  304 call runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak13,ak23,ak33,ak43,x13,
     $x23,x33,t3,tc3,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,
     $gam2,dfac,nc,tsc,dx3,corr1)
      dx1=(dz/6.)*(ak10+(ak11*2.0)+(ak12*2.0)+ak13)
      x1=x1+dx1
      dx2=(dz/6)*(ak20+(ak21*2.0)+(ak22*2.0)+ak23)
      x2=x2+dx2
      dt=(dz/6)*(ak30+(ak31*2.0)+(ak32*2.0)+ak33)
      t=t+dt
      dtc=(dz/6)*(ak40+(ak41*2.0)+(ak42*2.0)+ak43)
      tc=tc+dtc
      tctr=t+(t-tc)*0.25*biot/(1+0.25*biot)
      x31=x3
      nt1=nt
      dx3=0.
      ni=0.
      w=0.
      dw=0.
 320  w = w + dw
      kwgs = exp(3.296-(9170./1.987*(t-600.)/(600.*t)))
      af = (kwgs*(pH2O-w)*(pCO-w))-((pCO2+w)*(pH2+w))
      dfdw = -((kwgs*(pH2O-w))+(kwgs*(pCO-w))+(pCO2+w)+(pH2+w))
      dw = -af/dfdw
      ni=ni+1
      if (af.gt.0.001) goto 320
      pCO2=pCO2+w
      pH2=pH2+w
      pCO=pCO-w
      pH2O=pH2O-w
      nt=nt0-2*x1+x2/nc
      x3 = pCO2*nt/pt
      dx3= (x3-x31)
      ct=t-273
      ctc=tc-273
      ctctr=tctr-273
      if (kk.lt.50) goto 325
      nn=nn+1
      vct(nn)=ct
      vctc(nn)=ctc
      vdt(nn)=vct(nn)-vctc(nn)
      vz(nn)=z
      vctctr(nn)=ctctr
      vpCO(nn)=pCO
      vpH2(nn)=pH2
      vpM(nn)=pM
      vpHC(nn)=pHC
      vpH2O(nn)=pH2O
      vpCO2(nn)=pCO2
      vpMeq(nn)=pMeq
      vU(nn)=U
      vx1(nn)=x1
      vx2(nn)=x2
      vx3(nn)=x3
      va(nn)=a
      vb1(nn)=b1
      vb11(nn)=b11
      vb111(nn)=b111
      vc(nn)=c
      vd(nn)=d
      ve(nn)=e
      vcpc(nn)=cpc
      vcpgas(nn)=cpgas
      vhout(nn)=hout
      vaw(nn)=aw
      vker(nn)=ker
      kk=0
      if (t.gt.1000) goto 390
      if (tc.gt.1000) goto 390
  325 if (z.lt.zt) goto 200
      goto 390
  340 write (1,*) 'Enter output address for tables printing:'
      write (1,*) '      Screen:1 ; Printer:6'
      read (1,*) N
      write(N,344)
  344 format('1',//,29x,'TEMPERATURE PROFILES',//)
      write(N,342)
  342 format(17x,'  z    ',7x,' T     ',8x,'Tc     ',6x,'T-Tc',
     $//)
      do i=1,nn
      write (N,343) vz(i),vct(i),vctc(i),vdt(i)
  343 format(17x,f5.3,7x,F6.2,7x,F6.2,6x,f6.2)
      end do
      goto 450
  390 nt=nt0-2*x1+x2/nc
      xgaso=xC5+xC6+xbe+xto+xxy+xtri+xtmb
      xHC=xC1+xC2+xC3+xC4+xgaso
      pflow=(nt*(1-(xgaso/xHC*pHC/pt))*24200/60)
      anCO=(pCO/pt)*nt
      conCO=(nCO0-anCO)/nCO0*100
      anH2=(pH2/pt)*nt
      conH2=(nH20-anH2)/nH20*100
      tt=pM+pHC+pH2O+pCO2
      ppCO2=pCO2/tt*100
      ppH2O=pH2O/tt*100
      ppHC=pHC/tt*100
      ppM=pM/tt*100
      ttt=ppM*32+ppHC*wm+ppH2O*18+ppCO2*44
      ppCO2=ppCO2*44/ttt*100
      ppH2O=ppH2O*18/ttt*100
      ppHC=ppHC*wm/ttt*100
      ppM=ppM*32/ttt*100
      wHC=(pHC/pt)*nt*wm*1000
      war=whc*td/60*wgaso
      write (N,375)
  375 format(7x,24'*',/,9x,'ESTIMATED PARAMETERS',/,7X,24'*')
      WRITE (N,376) ENTH1
  376 FORMAT(/,14X,'Enthalpy of reaction: ',f8.1,' Kcal/Kmol')
      write (N,372) corr1,corr2
  372 format(13x,'Preexponential factor: ',f5.2,/,9x,'Heat transfer coef
     $ficient: ',f5.1,' Kcal/m**2*h*K')
  610 write (N,391)
  391 format(//,7x,15'*')
      write (N,392)
  392 format(11x,'RESULTS')
      write (N,393)
  393 format(7x,15'*',/)
      ct=t-273
      write (N,394) ct
  394 format(9x,' Final product temperature: ',F6.2,' C')
      write (N,395) pflow
  395 format(9x,'        Final product flow: ',F5.2,' l/min')
      ctc=tc-273
      write (N,396) ctc
  396 format(9x,' Final coolant temperature: ',F6.2,' C',/)
      write (N,397) conCO
  397 format(9x,'             CO conversion: ',F4.1,' %')
      write (N,398) conH2
  398 format(9x,'             H2 conversion: ',F4.1,' %',/)
      write (N,399) ppCO2
  399 format(9x,'      Product distribution:     CO2   ',F4.1)
      write (N,400) ppH2O
  400 format(9x,'                                H2O   ',F4.1)
      write (N,401) ppHC
  401 format(9x,'                                HC    ',F4.1)
      write (N,402) ppM
  402 format(9x,'                                CH3OH ',F4.1,/)
      goto 340
  450 stop
      end
c
c
c*************************************************************
c     Subroutine runge contains the differential equations
c*************************************************************
c
c
      subroutine runge (a,a1,a2,b1,b11,b111,b2,c,d,e,ak1,ak2,ak3,ak4,x1,
     $x2,x3,t,tc,pt,pCO,pH2,pM,pH2O,pHC,pCO2,nCO0,nH20,pMeq,gam1,gam2,
     $dfac,nc,tsc,dx3,corr1)
      real keq,nCO0,nH20
      ak=1.5
      keq=exp(-(54.15-21660/t)/1.987)
      x1e=0.
      pM0=pM
```

```
500 af=pt**2*(nCO0-x1e)*(nH20-2*x1e)**2*keq-x1e*(nCO0+nH20-2*x1e)**2
    dfdx1e=-(pt**2*(nH20-2*x1e)**2*keq+4*pt**2*(nCO0-x1e)*(nH20-2*
   $x1e)*keq+(nCO0+nH20-2*x1e)**2+4*x1e*(nCO0+nH20-2*x1e))
    dx1e=-af/dfdx1e
    x1e=x1e+dx1e
    pMeq=pt*x1e/(nCO0+nH20-2*x1e)
    dpMeq=abs(pMeq-pM0)
    if(dpMeq.lt.0.001) goto 510
    pM0=pMeq
    go to 500
510 pCO=pt*(nCO0-x1-x3)/(nCO0+nH20-2*x1+x2/nc)
    pH2=pt*(nH20-2*x1+x3)/(nCO0+nH20-2*x1+x2/nc)
    pM=pt*(x1-x2)/(nCO0+nH20-2*x1+x2/nc)
    pHC=pt*x2/nc/(nCO0+nH20-2*x1+x2/nc)
    pH2O=pt*(x2-x3)/(nCO0+nH20-2*x1+x2/nc)
    pCO2=pt*x3/(nCO0+nH20-2*x1+x2/nc)
    t1=(1/t)-0.0015374
    aa=corr1*exp(-8340/1.789/t)
    bb=0.0329*exp(9682*t1/1.789)
    cc=0.0645*exp(8626*t1/1.789)
    ee=0.367*exp(1031*t1/1.789)
    rCO=((aa*pCO*pH2**2)/(1+bb*pCO+cc*pH2+ee*pCO2)**3)
   $*3600*1E-6
    rH2O=(pM*exp((-a2/t)+b2))/(1.0+ak*(pM+pH2O))
    dx1dz=a*rCO*gam1
    dx2dz=a*rH2O*gam2
    dtdz=(b1*rCO)-c*(t-tc)+e*(2*rCO*gam1
   $-(rH2O*gam2/nc))
    dtcdz=d*(t-tc)
    ak1=dx1dz
    ak2=dx2dz
    ak3=dtdz
    ak4=dtcdz
    return
    end
```